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92-LLB-016

Mr. David B. Jansen, P.E.
Hanford Project Manager
State of Washington
Department of Ecology
P.O. Box 47600
Olympia, Washington 98504-7600

Dear Mr. Jansen:

RESPONSES TO ECOLOGY COMMENTS CONCERNING GAS GENERATION AT THE GROUT FACILITY

Enclosed are responses to comments concerning gas generation at the grout vaults (Enclosure 1). The comments were submitted in a letter dated August 26, 1991, from Mr. T. M. Michelena, State of Washington, Department of Ecology (Ecology), to Mr. C. E. Clark, U.S. Department of Energy, Richland Field Office (RL), with the following subject "Hydrogen Gas Generation at the Grout Treatment Facility." The comments were based on the review of a Pacific Northwest Laboratory (PNL) report by G. A. Whyatt titled "Gas Generation and Release From Double-Shell Slurry Feed (DSSF) Grout Vaults," PNL-7644. The gas generation issue originated from Notice of Deficiency Number 20 that was related to reactivity and ignitability of the grouted waste.

It is the position of the RL that PNL-7644 should not be expanded to include the evaluations and analyses requested in the State of Washington Department of Ecology's (Ecology) comments. PNL-7644 was intended to be a general document with emphasis on immediate design issues. We have discussed this with Ecology and they basically agreed, including concurring with our plans for the appropriate documentation.

The evaluations and analyses requested by Ecology will be developed and documented in separate supporting documents. These supporting documents will: (1) Expand the knowledge of gas generation and concentration issues, (2) analyze safety impacts, and (3) support conclusions arrived at in the Grout Safety Analysis Report (SAR) and the "Performance Assessment of Grouted Double-Shell Tank Waste Disposal at Hanford" (PA). The SAR will cover the operating periods, and the PA will cover the long-term post operating periods. When completed the SAR, PA, and supporting documents will be issued as publicly available documents.

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The following reports will be provided to Ecology when they are completed:

- "Grout Facility Safety Analysis Report" (SAR), WHC-SD-WM-SAR-042. The requirements for hydrogen monitoring and mitigating equipment given in the SAR will be implemented in the time frames required. Verification of the upper bounds of the model will be pursued by occasional hydrogen monitoring of the leachate sump vapor space at periods of not more than six months duration.

- "Grout Disposal Facility Compartment Gas Concentrations Report," WHC-SD-WM-ER-151. This report outlines gas generation rates and corresponding gas concentrations anticipated in the grout vault vapor spaces at different times.

A summary of the lightning mitigation design is enclosed (Enclosure 2) in response to Ecology's questions expressed in the November 12, 1991, Unit Manager's Meeting.

In addition, notes are enclosed (Enclosure 3) that support the contention that the waste does not have ignitable or reactive characteristics, as requested in the October 6, 1992, Unit Manager's Meeting.

If you have any questions regarding this transmittal, please contact L. A. Huffman of my staff on (509) 376-0104.

Sincerely,

S. H. Wisness
Hanford Project Manager

DSD:LAH

Enclosures:
1. Responses to Comments to PNL Report 7644
2. Lightning Mitigation Design
3. Ignitable or Reactive Characteristics

cc: R. E. Cordts, Ecology, w/encl.
T. M. Michelena, Ecology, w/encl.
J. A. Voogd, WHC, w/o encl.
B. A. Austin, WHC, w/encl.
D. Duncan, EPA, w/encl.

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RESPONSES TO ECOLOGY'S COMMENTS TO PNL REPORT 7644, GAS GENERATION AND RELEASE FROM DOUBLE-SHELL SLURRY FEED (DSSF) GROUT VAULTS

The purpose of the 1991 Whyatt report on "Gas Generation and Release from Double-Shell Slurry Feed (DSSF) Grout Vaults" was to take the first look at the possibility of gas generation from the grout in the vault, and resulting potential concerns. The purpose of the report was also to make some recommendations to alleviate potential concerns during a time when the grout vaults were in construction and could still be easily modified, and to suggest further investigations which would clarify potential concerns.

The purpose of the report was not to perform a safety analysis, or to document the final analysis of potential gas concern mitigation. Normally a safety analysis is performed on the facilities to establish the risk and consequence of potential concerns. In this case it is the Grout Facility Safety Analysis Report (SAR) WHC-SD-WM-SAR-042, which will become a public document. The SAR may contain analysis of risk and consequence of combustible gases, or reference documents that have the detailed analysis. Currently a detailed analysis is ongoing that will determine the risk of the situation and model the mitigating features that are necessary. References in the SAR may not include the Whyatt report if it is not applicable. The mitigating engineering features will be documented in Engineering Change Notices (ECN) which will be provided to Ecology as necessary.

The Grout Performance Assessment (PA), WHC-SD-WM-EE-004, is the document which analyzes long term environmental impacts after the vault is closed. This document will analyze the effects of gas generation on the grout vault system and the environment, if it is determined to be a concern.

Airborne radioactive and organic emissions are covered in the "Grout Treatment Facility Airborne Emissions Projections", WHC-SD-WM-TI-427. Note the "Application for Approval of Modification for the Grout Treatment Facility" pursuant to 40 CFR, Section 61.07 (NESHAP) was approved.

It is felt that the Whyatt Report served its intent, and that there would be little use in revision of a report which will soon be supplemented by more diverse and detailed reports and analysis. Therefore the Whyatt report will not be revised at this time.

Summary

1. Summary, Page iii, Paragraph 2

Deficiency:

The text states hydrogen gas is produced by radiolytic decomposition of water, but must be vented. The report recommends that a static diffusion barrier be employed without a venting. The report also indicates that additional tests would be required to determine the validity of this recommendation. This approach appears to be unproven and untested and is not specific.

Recommendation:

This recommended venting system should be defined, and an illustration included.

Response:

The Whyatt report recommends "that a passive approach to hydrogen venting be pursued to show that the hydrogen can diffuse through the diffusion barrier without the presence of a vent." This statement means that the asphalt diffusion barrier will probably release enough gas through it to make any additional vent unnecessary. The report recommends that more studies be performed to determine if this is the case. The studies are not necessary if vents are installed, or if it is determined that cracking of the asphalt diffusion barrier is acceptable. The revised PA now models a cracked barrier and finds it acceptable.

The report goes on to say that if a passive approach to venting is not feasible, it is recommended that a vent be installed. Because it could not immediately be proved that diffusion of the hydrogen out of the vault is adequate, two small vents were incorporated into the design. The vents are shown in Engineering Change Notice (ECN) 71 to Project B-714. Additional calculations show that the installed vents are sufficient to reduce the bounding case projected gas flows to acceptable values, less than about 10 psi differential pressure, which will prevent cracking of the asphalt barrier.

2. Summary, Page iii, Paragraph 3

Deficiency:

The report suggests an alternative small gas venting tube be installed through the diffusion barrier described above. There is no mention of the potential for water vapor condensation plugging the very small diameter venting tube located only one place in the vault. There is no process flow diagram or illustration of this gas venting system.

Recommendation:

The proposed alternative gas venting system is probably inadequate for the application. Vent tubes should be larger in diameter than those proposed in order to reduce the gas generation back-pressure and any moisture condensation problems. A process flow diagram or a system illustration should be presented (or referenced to a similar one presented later in the report.)

Response:

One 0.1-in. I.D. vent line was the minimum recommended number and clear opening. A tube with this opening and the expected maximum generation rate produces a pressure drop over 6 feet of line of only 2.2E-4 psi. The actual vent line design consists of 2, 1/4-in. (0.18 in ID) vents approximately 12 feet long from the catch basin. If both of these tubes were to become completely filled with water, the back-pressure to maintain a volumetric flow of 20.6 ft^3/d is only 1.03 psi. Of this pressure drop, only 0.17 psi is due to frictional pressure drop; the remainder is due to the elevation change from entrance to exit of the vent. The vent design is shown in ECN-71.

3. Summary, Page iii, Paragraph 4

Deficiency:

The text states that the rate of gas generation will be low enough so that after 250 years, the vault can be closed and the hydrogen gas can be reduced through the porous asphalt diffusion barrier. No mention is made of other gases which could be generated, or at what rates they might be generated.

Recommendation:

The text should address the issue of radiolytic hydrogen which can be generated from the decomposition of water (H_2O) as well as from the decomposition of tritiated water (HTO). Radon gas and volatile organic vapors may be generated in the vaults as well. There should be a statement of what variabilities of gas venting rates might be experienced after 250 years.

Responses:

The most appropriate experimental evidence of gas generation composition and rates are noted in H. A. Friedman, L. R. Dole et. all, "Radiolytic Gas Generation Rates from Hanford RHO-CAW sludge and Double-Shell Slurry Immobilized in Grout", ORNL-TM-9412, June 1985. The document uses simulated DSSF and a grout formulation similar to that anticipated for the 106-AN campaign.

Hydrogen and nitrous oxide are expected to be the primary radiolytic gases generated. The total gas generation rate is expected to be very low, see Friedman 1985 and Comment 19.

Organic vapor production is expected to be very low due to the low concentration of organics in the waste feed and the lack of organic vapor from similar grout feed, Friedman 1985. All double-shell slurry feed (DSSF) has been processed by a moderate temperature vacuum evaporator. The evaporation was performed to reduce the volume of the waste. DSSF has normally been processed by the evaporator at least twice in becoming DSSF. Since volatile organics are not anticipated in greater than ppm concentrations in the feed and there are almost no organics in the dry materials, no significant organic vapors are anticipated.

The vents designed for the vaults are oversized in size and number, see Comment 2. These design modifications should prevent any destructive pressurization of the vault, but there is little effect if a small vent is opened, see the revised PA.

4. Summary, page iv, Paragraphs 1, 2

Deficiency:

The text mentions dose commitment rates for radon gas and tritium releases from the grouting vaults, but does not address the gas flow rates on which these estimates are made. It does not mention if any other radionuclide releases may occur from the grouting vaults.

Recommendations:

There should be a table constructed to show the following information: (See Table 1 on page 42 of Enclosure 1)

These two paragraphs should be combined and included in the text as one paragraph.

Response:

Radon: Release for radon and tritium are based on the maximum hydrogen generation rate. Other gaseous radionuclide releases are expected, but less than that modeled for hydrogen alone in the Whyatt report. More details on the tritium and radon calculations are found in the sections of the report entitled "Radon Generation and Release" and "Tritium Release." Radioactive release information has been provided to the state in air permit applications.

The volume of radioactive gases is negligible. The items below provide information equivalent to the requested table.

Under the assumption that the radium and radon are in equilibrium with the ^{234}U, the total amount of radon gas that can exist at one time in the grout, catch basin, soil, and atmosphere above a vault is 3.6E-9 moles or 2.9E-9 ft^3.

The release of tritium was estimated at 3.5E-10 mol/day or 1.0E-7 ft^3/year. Also see NESHAP air permit. The above information does not pertain to ignitable feed comment and is provided for information only.

5. Summary, Page iv, Paragraph 3

Deficiency:

The report states that there has been no identified need for a gas venting system to be used with the grouting vaults. This statement is in direct conflict with a statement made in the first sentence of Paragraph 5 on the previous page, which states that a potential hazard exists for explosive mixtures of hydrogen gas to accumulate in the soil near the vent and in the catch basin of the vault.

Recommendation:

The report should include the possibility of a dynamic gas venting system to remove hydrogen gas and other gases from the catch basins. Such a system would make it possible to state with confidence that there will be no hazard of explosion resulting from hydrogen gas accumulation in the system.

Response:

Two vents per vault have been added to the diffusion barrier design. These vents can be seen in ECN-71, Project B-714. These vents will preclude the possibility of destructively pressurizing the vault.

Paragraph 3, page iv states: "No need for vents in the closure cover of the vault has been identified." The closure cover is approximately 10 ft thick. The cover is composed of plastic, clay, earth, and sand which sits on top of a vault pair like the roof on an A-frame house. This closure cover does not require vents because the ends of the A-frame are open, and the hydrogen will diffuse out these ends. The diffusion barrier is a 19 to 40 inch thick asphalt and aggregate water vapor barrier, similar in composition to asphalt roads. Therefore, statements on page iii and iv are correct.

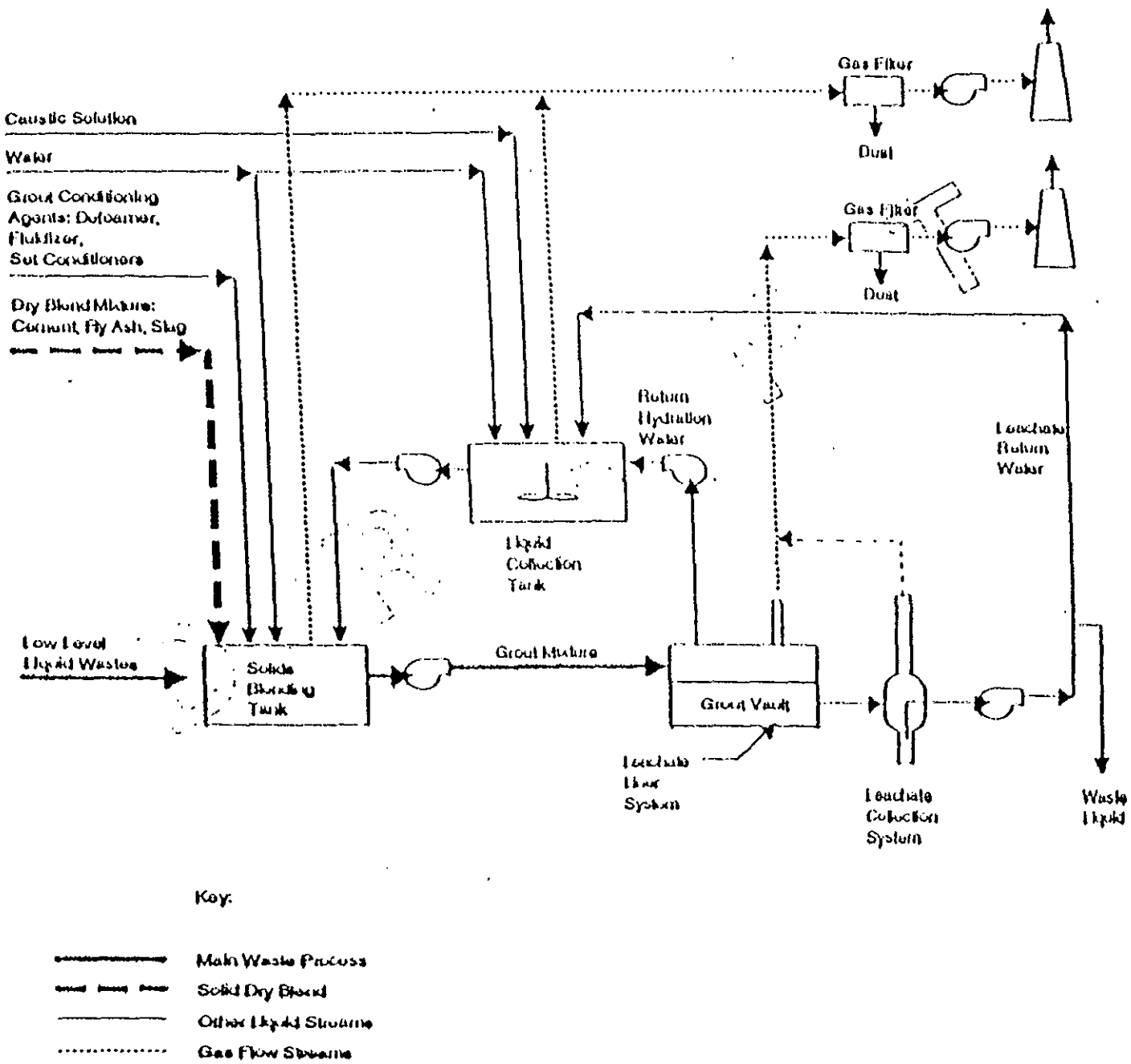
The work in question was not intended to be a safety analysis. This is beyond the scope of the ignitability question. Safety issues will be analyzed in the SAR.

Introduction

6. Introduction, Page 1, Paragraph 1

The text briefly describes the grouting vault design features, but it does not provide an illustration. It also does not show the potential points for gas release from the grouting vaults.

Figure 1: Process Flow Diagram of Grouting for Low-Level Waste Solidification Deficiency:



Recommendations:

A process diagram or illustration of the grouting vault configurations should be included, such as shown on the enclosed Figure 1. A separate discussion of gas release should be made, including how much gas is released and from where.

Response:

Vault design drawings were previously transmitted to Ecology.

There are three areas of interest for hydrogen gas build up and release. The first is the vault vapor space which is actively ventilated when the exhauster is operating and passively vented when the exhauster is not operating. The second area of interest is the LCDRS, which will be passively ventilated, with the option of an active ventilation system should it be necessary. The third area is the vault itself after the observation period is complete and the leachate sump is closed. This area is vented by two tubes extending from the catch basin to a graveled area and from there to the soil column.

The information is not critical to the report.

7. Introduction, Page 1, Paragraph 2

Deficiency:

The text mentions that the double shell slurry feed (DSSF) is mixed with a blend of blast furnace slag, fly ash, Portland cement, and calcium carbonate to form a grout material. It does not state in what proportions these materials are mixed or how much is to be produced. It also does not mention waste or grout compositions, or that several different types of wastes are to be processed of varying compositions.

Recommendations:

It should be explained that in each grout campaign, a given amount of waste is mixed with the grouting materials to form a certain quantity of grout. The compositions of the major types of wastes processed for DSSFs should be listed as well as the expected compositions for at least the following types of waste materials:

1. NCAW: Neutralized Current Acid Wastes
2. NCRW: Neutralized Cladding Removal Wastes
3. PFPW: Plutonium finishing Plant Wastes
4. CCW: Complexant Concentrate Wastes

The radioactive isotope concentrations and nonradioactive constituents in the final grout mixtures should be reported. This is especially true for cesium-137.

Response:

Wastes other than DSSF are beyond the scope of this document. Radioactive isotope concentration and nonradioactive constituents in the waste are shown in Table 2 and referenced (Hendrickson 1990). The waste feed characterization data and dry material formulation will be given to Ecology at least 30 days prior to operation of the facility, as noted in the Part B permit.

8. Introduction, Page 1, Paragraph 2

Deficiency:

The second part of the paragraph relates only to release of gases, but does not make a distinction between radioactive and nonradioactive gases.

Recommendation:

This paragraph should be two consecutive paragraphs. The text should state that gases can be released from the vaults through radiolytic decomposition, volatilization, and evaporation.

Response:

The scope of the report is to discuss the generation of hydrogen within DSSF grout vaults. The generation and release of radioactive gases is considered only to the extent that the hydrogen being generated facilitates their release. See the NESHAP documentation for more information.

The distinction between volatilization and evaporation is inconsequential.

Gas Generation

9. Gas Yield, Page 2, Paragraph 1

Deficiency:

There is no introductory paragraph describing radiolytic and nonradiolytic gas generation in this section.

Recommendation:

There needs to be an introductory paragraph stating that both radiolytic and volatilization processes can occur in the vaults which may result in the release of gases which could be either radioactive or nonradioactive in nature. The generation of each of these gases should be described individually and the applicable chemical reactions (outlined below) presented.

Hydrogen:

$$2H_2O \xrightarrow{H_R} 2H_2 + O_2$$

Tritium:

$$2HTO \xrightarrow{H_R} 2HT + O_2$$

$$2T_2O \xrightarrow{H_R} 2T_2 + O_2$$

Oxygen:

$$2H_2O \xrightarrow{H_R} 2H_2 + O_2$$

$$2NaNO_3 \xrightarrow{H_R} 2NaNO_2 + O_2$$

Nitrous Oxide:

$$2NaNO_2 + H_2O \xrightarrow{H_R} 2NaOH + N_2O + N_2$$

Radon:

$$U_{238} \rightarrow U_{234} \rightarrow Th_{230} \rightarrow Ra_{226} \rightarrow Rn_{222}$$

Gases released by volatilization and evaporation from the grouting vaults, such as organic compounds, should be listed as well. These may be a special concern of the processing of complexant concentrate wastes (CCW) where relatively high levels of organics exist to produce the double shell slurry feed (DSSF). The releases of the volatile organic compounds (VOCs) are a concern as potential air toxins and as precursors of ozone formation under the recent Clean Air Act Amendments. These gases may have special permitting requirements.

Water vapor evaporation by means of volatilization from the grouting vaults also needs to be considered.

Response:

Trace gas generation from organic volatilization may be possible in addition to that from radiolytic processes. It is considered unlikely because Friedman did not report any organic vapors when grouted DSS mixes were irradiated. The volatilization of gasses such as nitrous oxide will be formed from organic materials in the grout and from heat generation of radioactive and chemical sources. Ongoing investigations will include identification and characterization of gasses produced by volatilization if they are significant.

The release of volatile organic compounds (VOC) from the grout facilities is expected to be far below allowable levels of release which are established by regulatory authorities. See approved NESHAP documentation. The initial feed content of VOC's are limited by 40 CFR268 land disposal restrictions. Sampling for VOC's will proceed as outlined in WHC-SD-RD-019, "Grout Treatment Facility Waste Feed Acceptance Criteria", and 40 CFR268.

The radioactive gasses generated in the grout facility are tritium and radon. Tritium will initially exist in the form of HTO which can become the more mobile form of HT by radiolytic decomposition. Radon is formed as a daughter product of transuranic isotope decay. See Comment 4 for further information.

10. Gas Yield, Page 2, Paragraph 2

Deficiency:

The report mentions hydrocarbon generation rates from pure water with cobalt-60. There is also reporting of hydrogen generation from both alpha and gamma radiation of pure water, but not from beta radiation. There is also no data presented on hydrogen generation from water as the result of the presence of cesium-137, which is considered to be the predominant radioisotope in the grout.

Recommendation:

There needs to be information assembled on the potential for radiolytic gas generation from the grouting vaults which could be assembled as shown in Table 2: (See Table 2 on page 42 of Enclosure 1)

Response:

In this case the generation rates caused by gamma radiation should be very similar to that from beta radiation. The report assumes that the yield from gamma and beta radiation are the same. The report does not neglect beta radiation. The results for combined beta-gamma radiation were completely consistent with those expected from low dose rate gamma radiolysis, see discussion by Dr. Meisel, page 50. This supports the use of data generated using gamma radiation as representative of actual waste.

Using the grout formulation anticipated with campaign 102, investigation of gas generation compositions predicts that the gas produced will be nitrous oxide and hydrogen. There is a low possibility of small amounts of oxygen and/or nitrogen. Gas generation rates will be very close to those reported by Friedman, 1985, for DSS.

11. Gas Yield, Page 2, Paragraph 3

Deficiency:

The radiolytic decomposition of water to produce hydrogen by means of beta radiation is a particular shortcoming. Data is not provided as an estimate of the possible contribution to the hydrogen generation from beta radiation as well as from alpha radiation. Later the report estimates are based solely on gamma emissions, which may be the least important.

Recommendation:

There is a degree of conflict present in the data for hydrogen gas generation, as shown in Table 3. (See Table 3 on page 42 of Enclosure 1)

Response:

It is believed that the generation rates caused by gamma radiation should be very similar to that from beta radiation. The report assumes that the yield from gamma and beta radiation are the same. It does not neglect beta radiation. Tests have been performed in which actual grouted waste was evaluated for hydrogen generation. The results for combined beta-gamma radiation were completely consistent with those expected from low dose rate gamma radiolysis. This supports the use of data generated using gamma radiation as representative of actual waste.

The degree of conflict statement is not clear. It is assumed that the degree of conflict is comparing literature values to the author's estimate. The "estimate" of 47.6E-13 mol/(g-rad) is discussed in Comment 12.

12. Gas Yield, Page 2, Paragraph 4

Deficiency:

This paragraph presents the rate of oxygen formation in the grout from limited experiments, but it does not balance stoichiometrically with the information previously presented for hydrogen gas generation.

Recommendation:

The total oxygen generation in the nitrate solution was up to 39.0×10^{-13} gm-mole per gm of water per rad irradiated. If 60 percent of the oxygen came from water irradiation, and 40 percent came from nitrate reduction, and there were two moles of hydrogen produced per mole of oxygen from water radiolysis alone, then the following hydrogen generation rates would occur:

$$H_2 \text{ generation} = (39.0 \times 10^{-13} \frac{gm \cdot mole\ O_2}{gm\ H_2O \cdot rad})(0.60\ \frac{water\ rad}{total\ rad})(2.0\ mole\ H_2)$$

This level of radiolytic hydrogen generation is much greater than previously reported, and is 12.9 times greater than the value used for making estimates

$$H_2 \text{ generation} = \frac{47.60 \times 10^{-13} \text{ gm·mole } H_2}{\text{gm } H_2O \cdot \text{rad}}$$

later in the report.

There is no breakdown of the hydrogen generation from radiolytic mechanisms from the different types of radiation for alpha, beta, and gamma. However, if the total estimates previously described were included, the balance shown in Table 4 could be obtained. (See Table 4 on page 42 of Enclosure 1)

These calculations should be verified by further data collection and analysis. It is important to emphasize that if the above data is correct, the radiolytic hydrogen generated from beta emissions is 2.42 times those of gamma radiation. The total hydrogen generated from all radiation emissions can be as much as 6.67 times that from gamma radiation alone.

Additional information will be required to either confirm or refute the above information. (See Page 3, Paragraph 1)

Response:

It is agreed that if hydrogen is stoichiometrically produced, the data presented by M. L. Hyder (1964) appears inconsistent with data for hydrogen generation provided by other sources. Although hydrogen probably was generated in a 2:1 stoichiometry, caution should be used before assuming this since the authors did not discuss any measurements of hydrogen generation. The experiments in which the source of oxygen was broken down into water and nitrate used a tracer (^{18}O) and a high dose rate (not provided) and assumed:

1. NO_2 yield at high dose rate is the same as at a low dose rate.

2. Published values for hydrogen yield.

This is confusing since the derived yield of hydrogen as presented in the comment of 46.8E-13 mol/(g rad) (corrected value from comment) is much greater than the values obtained for water irradiation of 4.5E-13 (Matherson and Ritter) or 3.E-14 mol/(g rad) (Friedman et al., 1985) 7.1E-13 (Gray and Simonson 1985). Data for nitrate solutions obtained by Matherson and Ritter show a maximum yield of 4.1E-13 mol/(g rad) with decreasing production at higher nitrate concentrations.

In general, when converting from the solution studied to the grout, the amount of material absorbing dose without gas generation is greatly increased, with the possible exception of high nitrate and nitrite solutions. In addition, the chemical environment is much different in grouts than in solutions. The maximum yields obtained from all sources in

which mortar was irradiated are less than 3.7E-13, which was the value selected as the yield value in the report.

Based on the inconsistency in comparisons to Hyder's results, and the greater similarity of the chemical environment in tests performed using mortars with simulated wastes, it is believed the value of 3.7E-13 selected for gas yield is reasonable and conservative.

Further investigation of gas generation composition has shown that nitrous oxide is anticipated, with a low possibility of small amounts of oxygen and/or nitrogen. Gas generation rates will be very close to that tested by Friedman, 1985 for DSS. These anticipated rates are in the order of 30 times less than the bounding case generated above. Due to the anticipated grout formulation being almost the same as that studied in Friedman 1985 it qualifies as appropriate experimental data. This is expanded further in ongoing studies for the SAR. In addition gas generation rates will be experimentally confirmed for the Vault 102 campaign, and when ever the formulation changes significantly.

13. Gas Yield, Page 3, Paragraphs 2, 3

Deficiency:

Data on gas generation is presented from two different sets of tests for grout as described by Bibler (1978) and Friedman (1985). In one set of tests, a modest amount of hydrogen gas was found along with a very small amount of nitrous oxide and essentially no oxygen. Other tests reported by Friedman indicated larger amounts of nitrous oxide than hydrogen generated with essentially no oxygen produced.

Recommendation:

The potential discrepancies between these two sets of tests need to be resolved with the results as shown in Table 5, as follows: (See Table 5 on page 43 of Enclosure 1)

The other information presented indicates that several variables can affect the types and amounts of gases generated from the grout by radiolytic means, as follows: (1) grout composition--especially reductive blast furnace slag; (2) grout temperature; (3) irradiation times; (4) irradiation intensity; (5) type of irradiation--alpha, beta, or gamma; and (6) ionic contents--chloride, nitrite, and nitrate, especially.

The irradiation of grout mixtures with alpha or beta emissions will probably generate much greater quantities of hydrogen gas than with gamma emissions alone. Alpha emissions will also tend to increase oxygen formation in contrast to gamma emissions. Temperature along with irradiation time and intensity will create a time-sensitive hydrogen gas generation system.

A more likely representative gas generation composition from grouting is estimated as follows: (See Table 6 on page 43 of Enclosure 1)

Response:

The uncertainty of gas generation is being addressed through bounding calculations and ongoing investigations to better define gas generations rates and compositions. These will be referenced in the Grout SAR when completed.

It is agreed that grout formulation, ionic contents (waste), and to some extent type of radiation will have an effect on the amount and composition of gas generated.

The effect on gas generation from different radiation sources are noted by Dr. Meisel. (See pages 50-52 of Enclosure 1). The discussion applies not only to liquid solutions in tanks but also (generally) to grouts. His conclusion is that alpha emissions cause higher generation rates than beta and gamma emissions, but that there are an insignificant amount of alpha emitters in the tank, and in this case in DSSF grout. The G values from gamma and beta emissions can be considered equal, and are well represented by the Co60 source used to irradiate the samples.

Friedman 1985, reports on a irradiated grout very similar to that anticipated in the 106-AN campaign, and a waste composition very similar to that in the 106-AN tank. Friedmans' gas rates and compositions were used as a basis for gas generation rates and compositions in ongoing studies. This information is applicable experimental test data.

Other variables, such as grout irradiation times, and intensity are thought to have more of a secondary effect on radiolytic grout gas generation, see Friedman 1985. Tests have shown that G(H2) does not change significnatly over temperatures between 22 and 100 degrees C, see Friedman 1985 and Bibler 1979. The current gas generation models of the grout vaults indicate that the effect of times and intensities will probably affect gas holdup in the grout mass.

Experimental testing of grouts is currently considered to be the best determination of gas composition and generation rates. This avenue will be pursued with different grout formulations and waste compositions as necessary.

14. Gas Yield, Page 4, Paragraph 1

Deficiency:

The gas generation rate of 3.7×10^{-13} gm-mole per gm material per rad may be too low for reasons previously cited, especially because gamma radiation is

the only source being considered. Calculated or estimated variations in gas generation rate are only defined in general terms of time and other process variables. The assumptions used in estimating the gas generation rates are only stated generally, and not presented in one place in a concise fashion.

Recommendation:

The average, maximum, and minimum values for gas generation reported from Table 1 of the report text (not this document) are as follows:

Average: 2.68×10^{-13} gm-mole/gm material-rad

Maximum: 23.20×10^{-13} gm-mole/gm material-rad

Minimum: 0.14×10^{-13} gm-mole/gm material-rad

The assumptions used in making the estimates of gas generation from the grouting vaults are as follows:

1. The dry blend material contains 28 percent by weigh of blast furnace slag.

2. The input waste material contains appreciable amounts of nitrate ion.

3. Only gamma radiation of the grout contents is being considered in the analysis.

The following items are not considered and/or specified in the analysis of the degree of gas generation from the grouting vaults:

1. The temperature in the vaults as a function of both space and time; expected changes in temperature are shown on Figure 2.

2. The actual composition of the dry blend material added to the waste in terms of the following constituents:

   a. Portland cement--type and amount
   b. Fly ash residue--type and amount
   c. Pottery clay--type and amount
   d. Attapulgite matter--type and amount
   e. Other materials--type and amount

3. The anionic contents of the grout in terms of the following:

   a. Nitrogen--nitrite, nitrate
   b. Sulfur--sulfite, sulfate
   c. Carbon--carbonate, bicarbonate
   d. Halogen--chloride, fluoride

e. Phosphorus--phosphate
f. Other anions

4. The cationic contents of the grout in terms of the following:

a. Monovalent--sodium, potassium
b. Divalent--Calcium, magnesium
c. Trivalent--aluminum, iron
d. Trace metals
e. Other cations

5. The actual radionuclide contents of the grout as follows:

a. Alpha emissions
b. Beta emissions
c. Gamma emissions

6. The effects of changes in waste type on the above factors:

a. NCAW--Neutralized Current Acid Waste
b. NCRW--Neutralized Cladding Removal Waste
c. PFPW--Plutonium Finishing Plant Waste
d. CCW--Complexant Concentrate Waste

7. The moisture content of the grout.

8. The solids content of the mixture.

9. Material balances on the grout-dry blend mixtures.

At the completion of the discussion of N_2O generation, break this paragraph. It would also be helpful if diagrams of the effects of specific process variables on the gas generation rate in terms of time could be included, as follows:

1. The effect of temperature on gas generation rate, as shown on Figure 3.

2. The effect of nitrate-nitrite ion content on gas generation rate, as shown on Figure 4.

3. The effect of chloride ion content on gas generation rate, as shown on Figure 5.

4. The variation in gas generation rate with respect to time, as shown on Figure 6.

The gas generation rates reported are not broken down into individual constituent gases, such as:

1. Hydrogen--H_2
2. Oxygen--O_2
3. Nitrogen--N_2
4. Nitrogen Oxides--N_2O, NO, NO_2
5. Tritium--T_2 or T_2O
6. Water vapor
7. Volatile organic compounds

Response:

The estimated gas generation rate is considered very high for the grouts and DSS compositions noted in Friedman, 1985. Actual hydrogen gas generation rates are expected to be much less.

Gas generation rate over time should track the decay in radiation fairly closely. Data presented by Lewis and Warren (CONF-891129-2) indicates that hydrogen generation rates decrease with increasing temperature from ambient temperature up to 120°C. Gray and Simonson (1985) also tested for the variation of gas production due to gamma irradiation of Permian basin brine and found a significant decrease in gas production with increasing temperature over a range of 75°C to 150°C. Therefore, neglecting the elevated temperatures at various positions and times after pouring of the grout is considered to be conservative.

For articles where a data set of several conditions was presented, the values listed in Table 1 represent the maximum generation rate reported in that source.

Gas generation rates will be broken down into individual gases in future work now in progress. There is anticipated to be nitrous oxide, hydrogen, and a small possibility of oxygen with the DSSF waste and 3 component grout similar to that found in Friedman, 1985.

The scope of the report is limited to double-shell slurry grout vaults. Therefore, it is not appropriate to discuss other waste feed streams at this time.

15. Gas Generation, Page 5, Table 1

Deficiency:

The data in Table 1 listing alternative sources of literature references for radiolytic gas generation needs to be more clearly organized.

Recommendation:

A revised Table 1 is presented as Table 7. From this reorganization, several conclusions can be made with regard to the effect of process variables on the gas generation process. These conclusions are listed:
(See Table 7 on page 44 of Enclosure 1)

1. The generation of radiolytic gases is much greater with alpha radiation than for gamma radiation.

2. There are no values reported for the effect of beta emissions on radiolytic gas generation.

Figure 2: Typical Ranges In Temperature Increases of Grouted Vault Mixtures

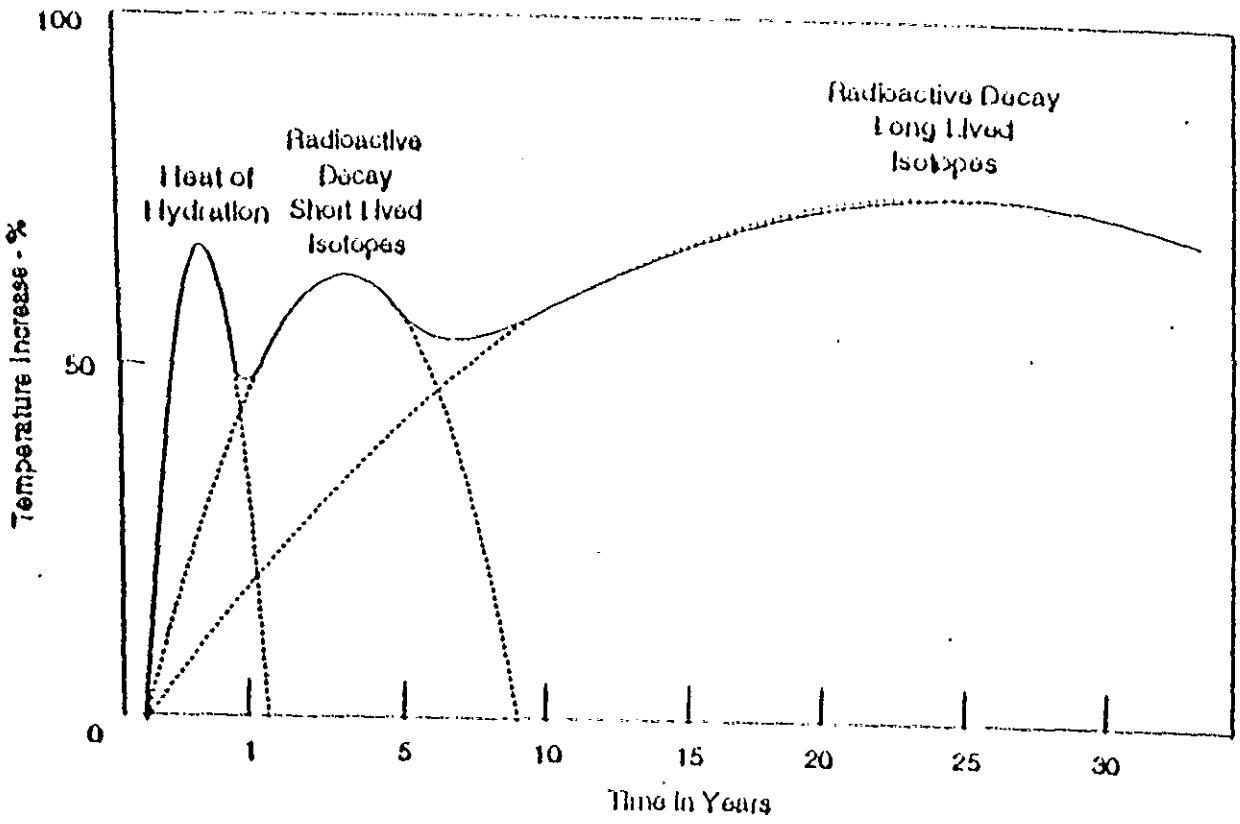
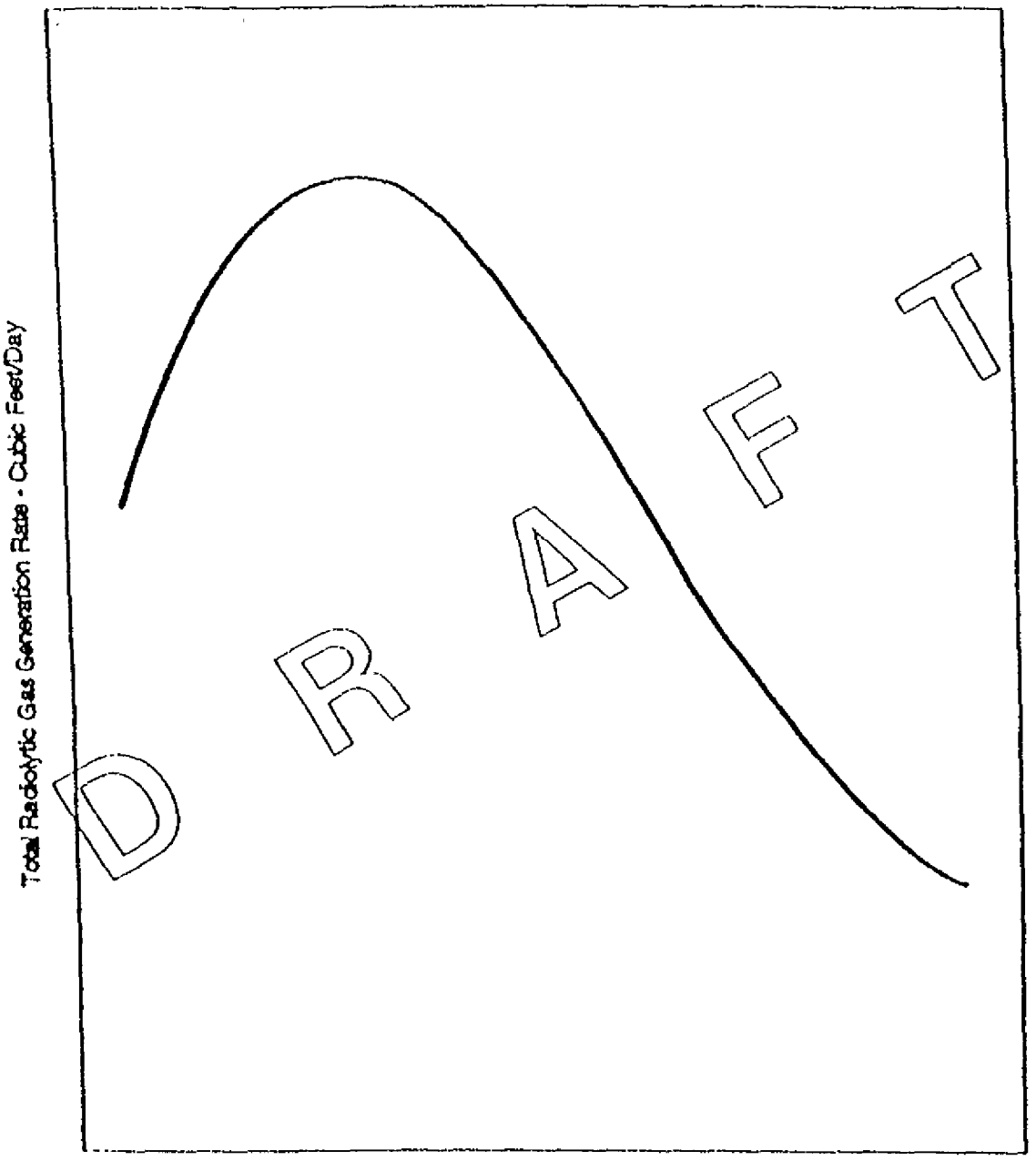
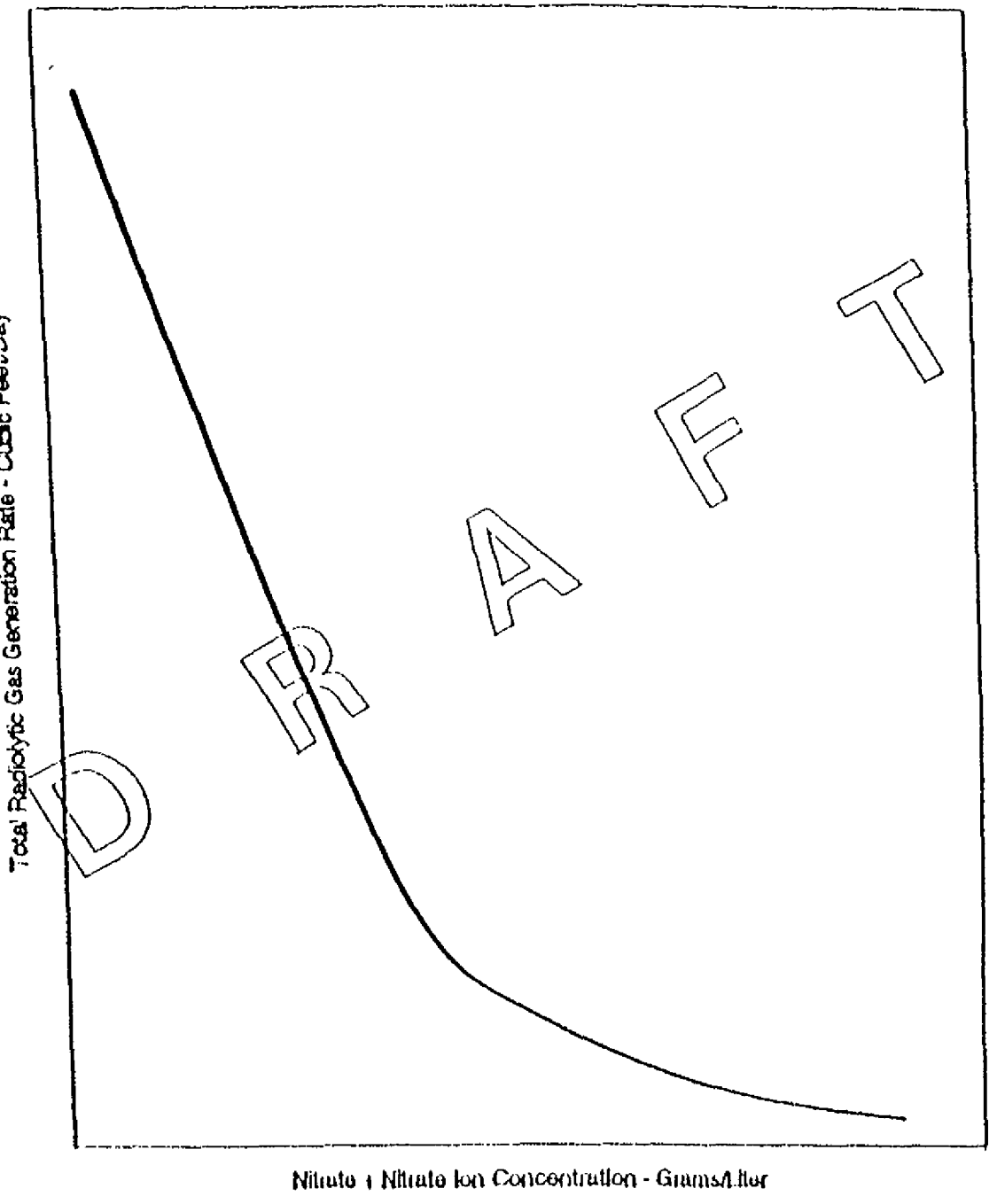


Figure 3: Effect of Grout Temperature on Radiolytic Gas Generation



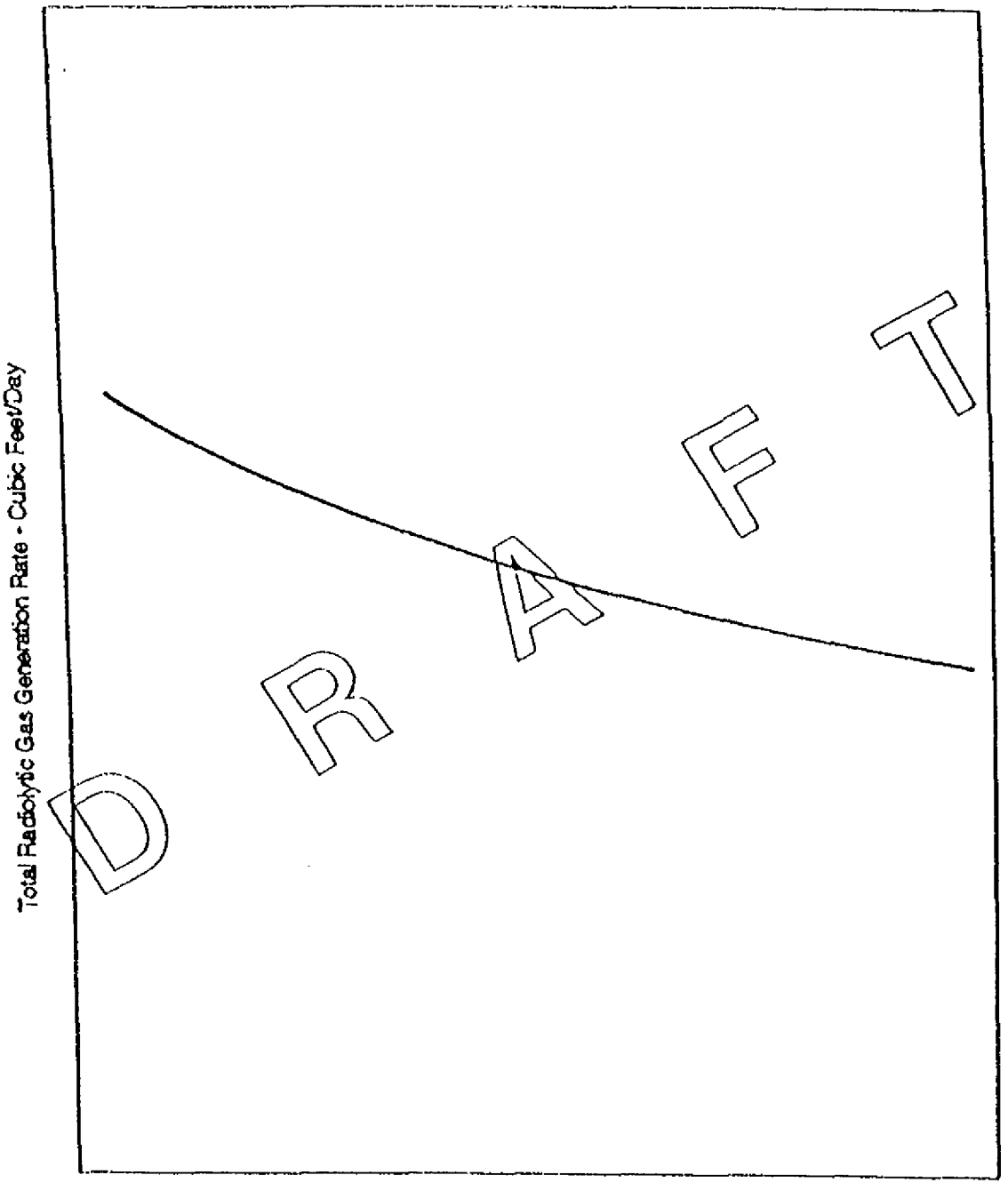
9 3 1 0 2 2

Figure 4: Effect of Nitrate Ion Content on Radiolytic Gas Generation During Grouting



9 3 1 2 3 0 2 3

Figure 5: Effect of Chloride Ion Content on Radiolytic Gas Generation During Grouting



9 3 1 2 2 0 2 4

3. The generation of radiolytic gas was greater in water than in solid grout mixtures, as noted below in Table 8. (See Table 8 on page 44 of Enclosure 1)

4. The increase in temperature ultimately acts to reduce the rate of radiolytic gas formation.

5. The increase in nitrate concentration of the media form acts to consume oxygen and reduce the rate of gas generation.

6. Increases in the chloride content of the grout tends to reduce the rate of radiolytic gas generation.

Response:

For articles where a data set of several conditions was presented, the values listed in Table 1 of the Whyatt report represent the maximum generation rate reported in that source. If it is necessary, measurements of specific grout material mixtures will be made which will be more representative and less conservative.

16. Dose Rate Determination, Page 4, Paragraph 2

Deficiency:

The initial dose rate from the grout mixture simulation is listed as 310 rads/hours. It is presumed that this calculation is based on the initial radioactivity level of the simulated grout, but it is not specified. There is nothing regarding the impact of varying types of waste formulations on the radioactivity load of the grout mixture for the four main types of waste materials.

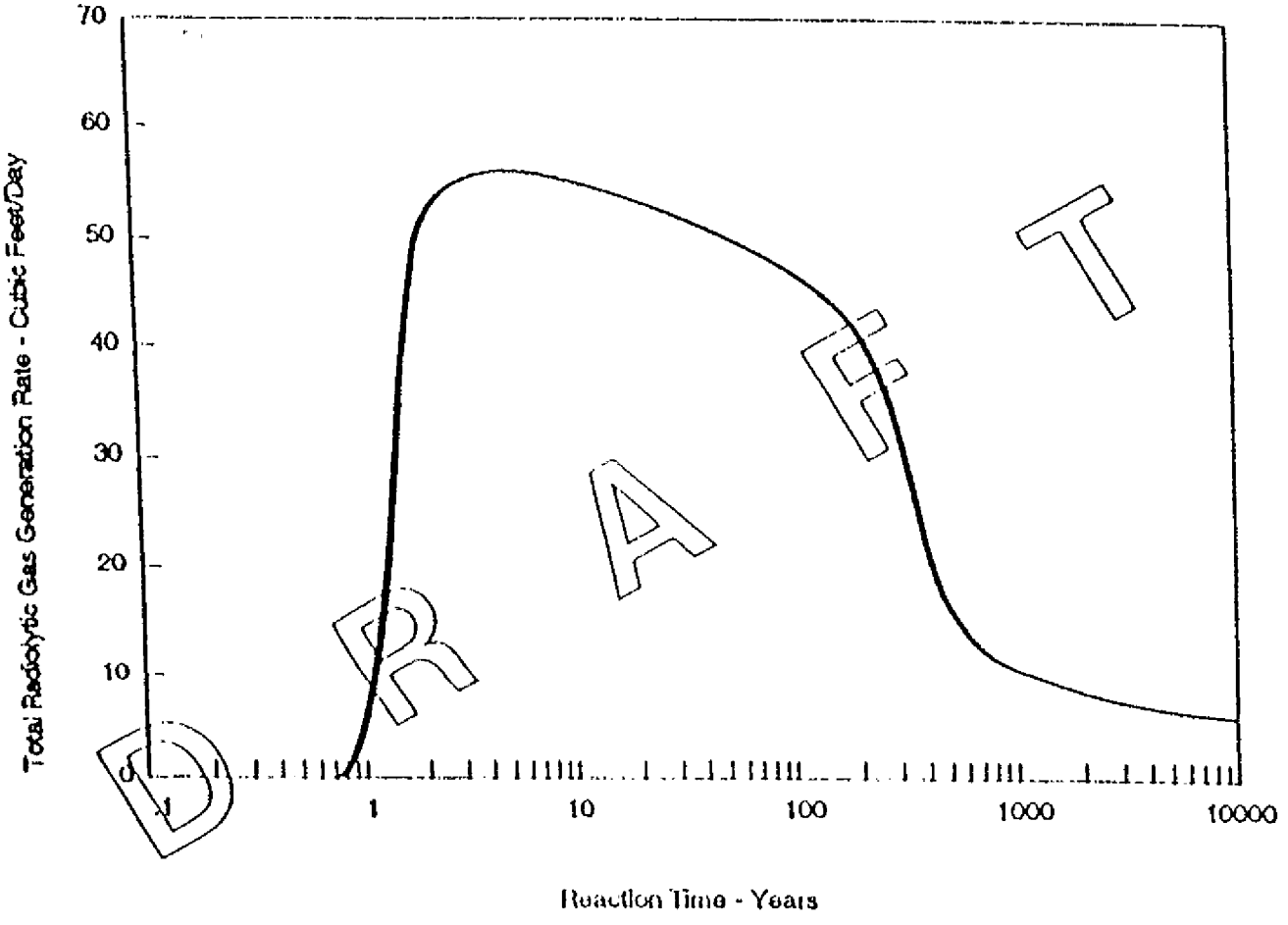
Recommendation:

The data for Table 2 could be reorganized into two separate tables. One of these tables could list the physical parameters (see Table 9). The second table could list the radioactivity levels at the starting time and after 30 years, along with the integrated dose commitment (see Table 10). A third table could present information for the different types of waste formulations (see Table 11). It would be helpful to plot the radioactivity level in the grout over time for each of the actual types of grout wastes to obtain an overall profile by using the existing Figure 2 in the text.

Response:

The additional information requested in the format of Tables 9 and 10 may be helpful, but it is not necessary in this document. Decay constants and gamma energy information is present within many references (e.g. as described by Table 9). The activity of any waste isotope is just as easily accounted through the simple calculation of:

Figure 6: Effect of Reaction Time on Estimated Radiolytic Gas Generation During Grouting



9 4 1 2 2 2 0 2 6

$$Activity_{(t)} = Activity_{(t=0)} * e^{-\lambda t}$$

where: $\lambda = 0.693/T_{½}$
$T_{½}$ = the half-life of the material in seconds,
t = the duration over which decay is evaluated [seconds].

This is the procedure of analysis as applied in response to comment 26. In that response, the polonium generated through the decay chain is evaluated by:

$$Po_{218}\ (g) = \left[\begin{array}{c} [N_{0,238} * (1-e^{-\lambda(238)t}) + N_{0,234}] * (1-e^{-\lambda(234)t}) \\ * (1-e^{-\lambda(230)t}) * (1-e^{-\lambda(226)t}) * (1-e^{-\lambda(222)t}) \\ * \frac{218\ g}{gmole} * \frac{gmole}{N_{Avg}\ nuclei} \end{array} \right]$$

where: The λ values used are those of the parenthesize parent isotope with the respective half-life. N_{Avg} is Avogadro's number of 6.022045 E+23 nuclei per gram mole.

The requested material is not required within this document and may easily be calculated by the reader should one be interested.

The third table requested is one of activity of varying waste streams upon disposal or at some final time. As discussed within the Dangerous Waste permit application, each waste type will be normalized by blending for radiolytic heat load. As such, the discussion of radiolytic loading presented within this document is expected to be relatively bounding for these materials independent of the waste type. Also note that the scope of the document covered only DSSF.

17. Gas Generation Rate, Page 5, Paragraph 1

Deficiency:

A relatively low value for radiolytic gas generation of 3.7×10^{-13} gm-mole per gram material per rad of emission is used for the calculations of radiolytic gas generation in the text.

Recommendation:

A bracketing of potential values for the quantities of radiolytic gas generation can be reported, as listed in Table 12. (See Table 12 on page 47 of Enclosure 1)

The gas generation rate used for estimating purposes is based on alpha and gamma emissions only. The predominant emissions are in the Beta mode for

the four radioactive isotopes constituting the predominant portion of the grout dosage, as shown in Table 13 for a previous study of other grout formulations. It is suggested that a value of 10.00 gm-mole of gas per gram of material per rad of dosage which is equivalent to a gas generation rate of 2.75 gm-mole per hour or 2.50 cubic feet per hour per vault would be more conservative. It is intermediate between the two average flow values reported. (See Table 13 on page 48 of Enclosure 1)

Response:

The value of 3.75-13 moles/g rad is considered to be a high (bounding case) for gas yield for our DSSF and projected grouts. If the composition of DSSF differs from that tested or if the grout formulation changes from that given in Friedman, 1985 then it will be necessary to experimentally determine actual rates using the new compositions. In any case the first DSSF grout vault waste composition and formulation "G" value will be experimentally determined. Also, note that gamma, beta and alpha radiation are included. The assumption made was that the yield value for each of the three radiation types was the same.

18. Hydrogen Migration Evaluation, Page 8, Paragraph 1

Deficiency:

The information provided on the equilibrium gas pressures lists several values for gamma radiation, a single value for alpha radiation, and no values for beta radiation. The reason for two equilibrium pressure values being reported for individual dosages is not explained.

Recommendation:

The does [sic] rate of the grout mixtures and the resulting equilibrium gas pressures need to be organized into a table such as Table 14 below. (See Table 14 on page 49 of Enclosure 1)

Response:

The equilibrium pressures represent pressures at which no more accumulation of gasses will occur with continued irradiation. These data are important in considering what will happen as gas is generated inside the grout mass. The equilibrium pressure is expected to be somewhat lower than the values reported in the literature where high dose rates are used in order to collect data in a reasonable time frame. If a pressure approaching the equilibrium pressure is maintained inside the grout pore structure, it could slow or stop the production of hydrogen. However, due to the uncertainty no credit has been taken for such pressures retarding the gas production rate. Instead, the maximum gas generation rate is assumed to be produced and the gas diffused to the catch basin.

The text is not considered to be deficient. The text states that "The equilibrium pressure changes with mortar composition ... " which explains why an identical dose rate produces different equilibrium pressures. The text presents all the information that is given in the recommended table. The recommended table is misleading in that it suggests that ranges of equilibrium pressures were measured (e.g., 20-40 psi for .10 rad/hr gamma) where in fact only the two values were reported.

19. Hydrogen Migration Evaluation, Page 8, Paragraph 2

Deficiency:

There is no discussion of the possible effects of oxygen gas generation simultaneously with hydrogen gas generation.

Recommendation:

A factor to consider is that oxygen is being produced at the same time that hydrogen is being produced under radiolytic decay conditions, as follows:

$$2\ H_2O + \text{heat} \rightarrow 2\ H_2 + O_2$$

Under significant grout temperatures and gas pressure in the vaults, there could even be the possibility that the two gases might recombine under potentially explosive conditions, as follows:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O + \text{heat}$$

It would be best to vent these gases at negative pressure by pumping rather than risking an explosive mixture under positive pressure in a manner similar to the so-called "burping" or "bumping" in the high level waste storage tanks, where gases are periodically released under surge conditions.

There is also no mention of the possible impacts of radiolytic hydrogen gas generation resulting from the presence of organic materials in the grout instead of from water. The matter is of particular concern from the complexant concentrate wastes containing appreciable proportions of radioactive wastes with an overall reaction:

$$C_x\ H_y\ O_z + \text{heat} \rightarrow CO_2 + H_2O + H_2 + O_2$$

Response:

The formation of oxygen gas does not occur directly from radiolytic decomposition of water. It may be formed by a secondary chemical reaction of hydrogen peroxide that is a direct product of radiolytic decomposition. The potential of oxygen formation and migration will be addressed by the grout facility design modeling now underway. Generally the production of oxygen is not expected. Tests by Friedman, 1985 indicated that oxygen was consumed during gamma radiolysis of the grouts containing the DSS solution.

Tests by Lewis and Warren (1989) in which blast furnace slag containing grouts were irradiated have shown that oxygen is consumed not produced.

The potential for gas generation from radiolytic decomposition of organic materials is also recognized, but it will be small due to the low concentration of organics in the grout feed, and the processing that the waste has undergone. See comment 3. Validation of the gas generation rates and compositions is planned.

Note that the grout vault will be filled only while it is actively ventilated. The burping of low-level waste tank SY-101 is a completely different mechanism, which applies to viscous organic liquids, not grouts.

20. Hydrogen Migration Evaluation, Page 8, Paragraph 3

Deficiency:

The text states that small "micro-cracks" could open in the grout from which hydrogen gas could be vented, and which would not be detrimental to the performance of the system. The exception is leaching from the liquid, which is not expected to occur. It does not describe liquid accumulation or gas accumulation in the grout.

Recommendation:

It might be advantageous to consider the use of aggregate materials in the grout which could act to increase its porosity upon solidification. The use of vertically aligned porous tubes in the grout could facilitate both drainage of condensate liquid to the bottom, and venting of entrained gas to the top of the grout mixture to prevent both gas release and liquid leaching.

Response:

As stated in the text, microcracking will allow hydrogen to vent from the grout more easily. Vertical tubes are not considered necessary. Aggregate within the grout formulation is not compatible with the process facility design.

21. Hydrogen Barrier Diffusion, Page 9, Paragraph 1

Deficiency:

The text states that the vault can become pressurized to 50 psi through an asphalt barrier, but does not show the asphalt barrier configuration of the vault.

Recommendation:

A diagram should be presented of the asphalt barriers in the grout vaults showing that the side barriers are 152.4 cm thick (60 inches) while the top and bottom layers are 96.5 cm thick (38 inches) with a surface area of 12,000,000 sq cm (12,917 sq ft). The pressure calculation of 50 psi assumes that there is no external venting in the grout vault.

Response:

Vault and cocoon design information has been presented to Ecology. The Appendix of the report gives the dimensions of the vault as 152.4 cm thick with an area of 1.1E7 cm2 and the vault top and bottom are 96.5 cm thick with and area of 1.2E7 cm2.

22. Hydrogen Barrier Diffusion, Page 9, Paragraph 3

Deficiency:

There is no direct estimate of hydrogen diffusion rate. There is no discussion of oxygen diffusion across the barrier. There is also no discussion of why the system may need to be vented to prevent accumulation of hydrogen or other gases or that only one vent per vault will be needed.

Recommendation:

If gas diffusion coefficients can be estimated from Fick's Law on the basis of differences in molecular weight, the rate of diffusion will increase with decreasing molecular weight according to the estimates shown in Table 15: (See Table 15 on page 49 of Enclosure 1)

Hydrogen should diffuse rapidly through the asphalt barriers of the grout vault if the above estimates apply.

An actual dynamic gas venting system for removing the hydrogen from the grout vaults, as shown in Figure 8, should be considered. The gas could be vented from the vaults and down through a central gas collection and treatment system built to serve several vaults at one time. The gas flow rate should be sized for several times the reported value of 1.01 gm-mole per hour, where a recommended value of 2.75 gm-mole per hour is suggested. A number of vents would be required, including vents for the space above the grout vault and the leachate control system vents.

Response:

Carbon dioxide literature values for hydrogen diffusion through the cocoon were used as a conservative estimate. Tests to determine the diffusion rate of hydrogen through asphalt are ongoing. Preliminary results from the tests show that the diffusion rates are faster, thus reducing the time frames and perceived capacities of the cocoon vents.

Forced exhaust on the leachate sump is being evaluated on an "as needed" basis after the operational phase (i.e., after cold capping). Preliminary gas concentration analysis results indicate that the leachate sump will only require passive ventilation after the operational phase to reduce hydrogen concentrations below the lower flammability limit. The HEPA filtered passive ventilation system depends on diffusion and atmospheric pressure changes to remove gas from the sump.

Additional gas treatment has been considered but is not needed, see Comment 28 response.

23. Hydrogen Vent Size, Page 10, Paragraph 3

Deficiency:

The hydrogen gas vent is sized for a gas flow rate of 1.01 gm-mole per hour, which is equivalent to a flow rate of 20.6 cu ft per day at 20°C and 1.0 atm with a 0.10 inch diameter for a 6-foot long section. This vent is not illustrated in the text.

Recommendation:

If the proposed vent were to be used, it should be sized for 2.75 gm-mole per hour or 56.6 cu ft per day with at least a 0.25-inch diameter. In addition, there should be porous vertical tubes placed in the grout with vent spaces at the top so that the gases can be removed. The vent should not go into the soil.

Response:

The expected "G" values are much lower than the bounding case values. In addition experiments will be conducted to confirm that the anticipated gas generation is within the lower limits analyzed for.

See responses to comments 2, 5, and 20. The design of the vent prevents blockage and mitigates flammability concerns by diffusing hydrogen into the soil, see ECN 71.

24. Vent Design guidance, page 12, Paragraph 2

Deficiency:

The vent tube of 0.1 inch diameter is not large enough and there should be more than one exhaust tube. In addition, there is no specification for what steps will be taken so "corrosion scale does not plug the opening of the vent."

Recommendation:

The vent tube size should be recalculated after gas generation rates have been adjusted based upon other technical comments in this assessment. Multiple tubes must also be addressed and the steps taken to prevent clogging must be specified. Furthermore, it would be appropriate to locate some tubes at higher elevations within the asphalt cocoon since the hydrogen gas which is generated will rise to the high points within the cocoon.

Response:

There are 2 vent tubes specified at .18 inch (ID) diameter, as noted in ECN-71 project B-714. Pressure gradients will drive the hydrogen out, no matter where the vents are located. Also see responses to Comments 2 and 5.

The SAR will evaluate the hazards and risks associated with the operation of the facility. There appears to be an incredible risk that a spark will be available in the grout vault to ignite the gas in the catch basin during and after the 30 year monitoring period. If it is necessary to mitigate the chances of such a spark occurring in a facility buried over 45 feet underground then the SAR and facility will require the appropriate equipment to be installed to prevent it, or make the risk incredible.

25. Potential Explosion Hazards, Page 13, Paragraph 1

Deficiency:

The gases generated are hydrogen, oxygen, nitrogen, nitrous oxide, tritium, and water vapor from the grout vaults, but flow measurements and compositions are not listed.

Recommendation:

Some delineation of expected volumetric composition of the grout vault gases should be made for the major types of waste. Hydrogen contents will be the greatest from the complexant concentrate wastes (CCW), where organic contents are highest. A flow-type gas venting system will help to reduce these explosion hazards.

Response:

Only DSSF waste will be evaluated at this time. The DSSF is expected to generate the composition and rates of gasses found in Friedman 1985. See previous comments.

The design (size and number) of the vents have been modified to the point that there is little chance that gas build up in the vault will destructively pressurize it. See Comments 2, 5 and 24.

26. Radon Generation Release, Page 14, Paragraph 3

Deficiency:

Radon release is quantified through the asphalt barrier, where it forms the solid polonium through decay. If the gas is vented, the aerosol can be released to the exhaust gas stream. No emission control systems other than soil filtration are planned.

Recommendation:

It is suggested that the radon gas be collected through a separate soil filter from the exhaust gas or an activated carbon adsorption system in a manner similar to that shown on Figure 8. Both the vapor space above the grout and the catch basin need to be vented to the gas collection and treatment system with slotted vents for some dilution with air to prevent the accumulation of explosive mixtures. A central gas collection and treatment system should be constructed to serve all 44 of the planned grouting vaults.

$$U_{238} \rightarrow U_{234} \rightarrow Th_{230} \rightarrow Ra_{228} \rightarrow Rn_{222}\ (gas) \rightarrow Po_{218}$$

Response:

As described in SD-WM-TI-355, Rev. 1, "Methods and Data for Use in Determining Source Terms for the Grout Disposal Program," the 95% confidence concentration of ^{238}U within the waste is 1.5955 E-08 Ci/L. The 95% confidence concentration of ^{234}U within the waste is 3.223 E-08 Ci/L. As presented in the following tables and graph, insufficient material exists for potential measurement, let alone capture, following transport through the soil column, during the first 300,000 years following disposal. No additional action will be taken in this regard.

27. Radon Generation Release, Page 17, Paragraph 2

Deficiency:

The text states that radon diffusion is not a concern from a human health standpoint.

Recommendation:

It would be a better approach to evaluate the effects of drawing the vault top and bottom gases through a central exhaust gas treatment and control system in comparison to the proposed system in terms of expected dosage levels. A better philosophical approach would be to make every effort to assure that potential problems do not occur rather than attempting to show that problems should not arise from the selected pathway.

Response:

The text was extremely conservative in the assumption that radon gas would achieve an equilibrium concentration of 8.34 E+06 pCi/ft^3. As developed for comment 26, one pico curie of radon-222 is equal to 3.077 E-11 g of radon. The stated equilibrium concentration would equal 2.57 E-4 g/ft^3, and at 26 ft^3/day would require the generation of 6.67 E-03 g/day of radon-222. As detailed in the tables of Total Target Material Generation, the first unit volume concentration of this amount could not be generated until approximately 3000-years following disposal. Figure 1 details equilibrium radon concentrations.

It is not credible to anticipate construction and operation of ventilation and control systems for periods greater than about 30 years. No additional action will be taken in this regard.

Initial Material Inventory and Decay Data

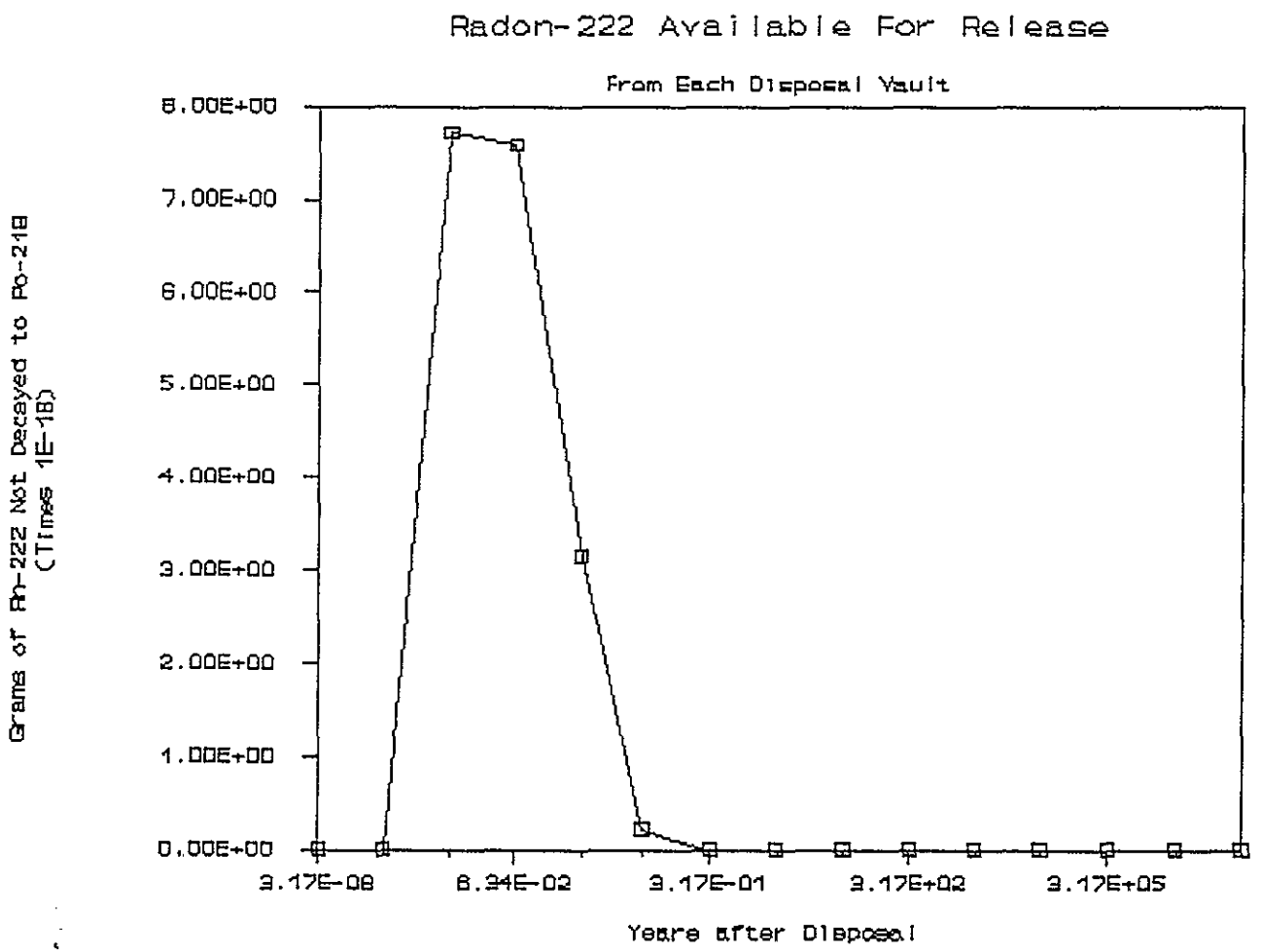
Radionuclide	Half-life		Half-life		Specific Activity (Ci/g)	Initial Activity (Ci/L)	Vault Activity (Ci)	Vault Nuclei [t=0]
238 U	4.468e+09	y	1.410e+17	s	3.36e-07	1.596e-08	6.039e-02	4.548e+26
234 U	2.454e+05	y	7.744e+12	s	6.22e-03	3.223e-08	1.220e-01	5.048e+22
230 Th	7.540e+04	y	2.316e+11	s	2.06e-02	0.000	0.000	0
226 Ra	1.600e+03	y	5.491e+10	s	9.89e-01	0.000	0.000	0
222 Rn	3.825e+00	d	3.305e+05	s	3.25e-02	0.000	0.000	0
						4.819e-08	1.824e-01	4.549e+26

Material Inventory (Nuclei) at Time (t) After Disposal								
t (years)	3.17e-08	3.17e-05	3.17e-02	6.34e-02	9.51e-02	1.58e-01	3.17e-01	3.17e+00
t (seconds)	1	1000	1e+06	2e+06	3e+06	5e+06	1e+07	1e+08
Radionuclide								
238 U	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.548e+26
234 U	5.048e+22	5.048e+22	5.048e+22	5.048e+22	5.048e+22	5.048e+22	5.048e+22	5.048e+22
230 Th	4.517e+09	4.517e+12	4.517e+15	9.034e+15	1.355e+16	2.259e+16	4.517e+16	4.516e+17
226 Ra	0.000	1.351e+04	1.351e+10	5.406e+10	1.216e+11	3.378e+11	1.351e+12	1.350e+14
222 Rn	0.000	0.000	2.095e+04	2.059e+04	8.534e+03	5.961e+02	0.000	0.000
Total	4.549e+26	4.549e+26	4.549e+26	4.549e+26	4.549e+26	4.549e+26	4.549e+26	4.549e+26

Material Inventory (Nuclei) At Time (t) After Disposal - Cont.							
t (years)	3.17e+01	3.17e+02	3.17e+03	3.17e+04	3.17e+05	3.17e+06	3.17e+07
t (seconds)	1e+09	1e+10	1e+11	1e+12	1e+13	1e+14	1e+15
Radionuclide							
238 U	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.548e+26	4.546e+26	4.526e+26
234 U	5.048e+22	5.046e+22	5.025e+22	4.820e+22	2.976e+22	3.558e+19	0.000
230 Th	4.504e+18	4.384e+19	3.349e+20	2.265e+20	4.373e+09	0.000	0.000
226 Ra	1.333e+16	1.174e+18	3.306e+19	1.416e+16	0.000	0.000	0.000
222 Rn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	4.549e+26	4.549e+26	4.549e+26	4.549e+26	4.548e+26	4.546e+26	4.526e+26

Total Target Material Generation									
Material Generated	t (years)	3.17e-08	3.17e-05	3.17e-02	6.34e-02	9.51e-02	1.58e-01	3.17e-01	3.17e+00
	t (seconds)	1	1000	1e+06	2e+06	3e+06	5e+06	1e+07	1e+08
222 Rn	Nuclei	0.000	0.000	1.706e+05	1.364e+06	4.605e+06	2.132e+07	1.706e+08	1.704e+11
	Moles	0.000	0.000	2.832e-19	2.266e-18	7.647e-18	3.540e-17	2.832e-16	2.830e-13
	grams	0.000	0.000	6.288e-17	5.030e-16	1.698e-15	7.859e-15	6.287e-14	6.283e-11
218 Po	Nuclei	0.000	0.000	1.496e+05	1.344e+06	4.597e+06	2.132e+07	1.706e+08	1.704e+11
	Moles	0.000	0.000	2.484e-19	2.232e-18	7.633e-18	3.540e-17	2.832e-16	2.830e-13
	grams	0.000	0.000	5.416e-17	4.865e-16	1.664e-15	7.718e-15	6.174e-14	6.170e-11
222 Rn Available	grams	0.000	0.000	7.723e-18	7.589e-18	3.146e-18	2.197e-18	4.915e-23	0.000

Total Target Material Generation - Cont.								
Material Generated	t (years)	3.17e+01	3.17e+02	3.17e+03	3.17e+04	3.17e+05	3.17e+06	3.17e+07
	t (seconds)	1e+09	1e+10	1e+11	1e+12	1e+13	1e+14	1e+15
222 Rn	Nuclei	1.692e+14	1.579e+17	8.374e+19	4.286e+21	4.307e+22	2.739e+23	2.280e+24
	Moles	2.810e-10	2.621e-07	1.390e-04	7.117e-03	7.152e-02	4.549e-01	3.787e+00
	grams	6.239e-08	5.820e-05	3.087e-02	1.580e+00	1.588e+01	1.010e+02	8.406e+02
218 Po	Nuclei	1.692e+14	1.579e+17	8.374e+19	4.286e+21	4.307e+22	2.739e+23	2.280e+24
	Moles	2.810e-10	2.621e-07	1.390e-04	7.117e-03	7.152e-02	4.549e-01	3.787e+00
	grams	6.127e-08	5.715e-05	3.031e-02	1.551e+00	1.559e+01	9.916e+01	8.255e+02
222 Rn Available	grams	0.000	0.000	0.000	0.000	0.000	0.000	0.000



: Radon-222 Generation Following Grout Disposal

28. Tritium Gas Release, Page 18, Paragraph 1

Deficiency:

There is no discussion of possible emission control systems available for tritium gas removal and recovery from the gas phase, or of a breakdown between tritiated water and tritium gas releases.

Recommendation:

Possible technologies should be evaluated for tritium gas recovery or incineration and for condensation of water in a central gas emission control system. Such a system might be suitable for a grouting vault exhaust gas collection and treatment facility for all 44 vaults. The dose assessment should also evaluate the worst-case on-site dose.

Response:

Technologies for collection of tritiated water were evaluated within the Grout Treatment Facility NESHAP Modification request to U.S. EPA Region 10 and emissions further defined in WHC-SD-WM-TI-427, Rev. 0, "Grout Treatment Facility Airborne Emission Projections." Tritium content of each vault is expected to be approximately 60 Ci, yielding a projected 44 vault total of 2,626 Ci. The specific activity of tritium is 9660 Ci/g. Thus, the expected total disposal of tritium is expected to be approximately 0.27 g over a 15 to 20 year period. Tritium is not generated within the waste or grout as these are not the environments of fusion reactions.

The most acceptable control method discussed within the NESHAP modification request was that of condensation. The drawbacks of such control are that the condensation could capture up to 2 million gallons of water per year and result in a control cost in excess of $12 Billion/ man-rem. Further, the NESHAP modification request detailed that the collected liquid could only be held in ventilated storage tanks, thus allowing the tritiated water to escape. The collected liquids, would in addition, be considered listed wastes and would require additional treatment equivalent to grouting. In net effect, the only "treatment" for tritiated water is radioactive decay.

As suggested by the comment, incineration was not considered as an acceptable treatment. The costs of incinerating vast quantities of water vapor are beyond any currently known BACT or LAER standards. In addition, such incineration would be of no effect as the radioactive nature of tritium is unaffected by incineration.

Dose models used in analyses detailed both on-site and off-site impacts. Tritiated water was used in analyses as tritium gas does not pose the same stronger exposure pathways of tritiated water. As a note, water

curtains are typically used to capture tritium gas through contact and conversion to tritiated water.

As each of the comments' pertinent points has been previously addressed and found to require no action, no additional action will be taken in this regard.

29. Closure Cover Vents, Page 19, Paragraph 1

Deficiency:

The text states that the need for venting has not been identified as a means of counteracting hydrogen gas buildup in the grouting vaults at a flow rate of 20.6 cu ft per day and accumulation in the soil. The text also states the venting is only necessary when pressurization is a concern. These statements are not correct, in our opinion.

Recommendation:

A gas venting system for the grouting vaults from both the vault top air space and the bottom liquid drain catch basin is advisable to prevent the possibility of the future occurrence of "grout burping" and also to alleviate the potential emissions of the following air pollutants:

1. Hydrogen gas
2. Tritium gas
3. Tritiated water
4. Nitrous oxide
5. Volatile organics
6. Particulate matter
7. Radioactive aerosols

The air pollution control system should consist of the following sections:

1. Particulate matter--filtration
2. Organics and radon--adsorption
3. Water and tritium--condensation

Response:

The Grout Facility has responded to this report by incorporating several vault design changes - adding a filtered vent to the LDCRS riser, a spark proof sump pump, and two vents through the asphalt barrier to the soil. The potential for actively ventilating the sump has been incorporated.

Hydrogen, tritium, nitrous oxide, water vapor and any organics which diffuse through the concrete will escape from the vault through the vents. Particulate matter and aerosols which are not water soluble will

not diffuse through the concrete walls of the vault structure. No further air pollution control system is envisioned, see comment 28.

30. Conclusions, Page 20

Deficiency:

The conclusions presented in the reviewed report are, in our opinion, deficient in terms of properly addressing the question of hydrogen gas generation and disposal.

Recommendation:

It is recommended that the conclusions of the report be rewritten to conform to the following:

Response:

The suggested changes are addressed individually below.

1. The rate of gas generation is estimated to be 10.20 gm-mole per gram grout per rad. The gas is expected to be composed of hydrogen with some oxygen, nitrous oxide, tritium, radon, and volatile organics. This value may be low for those wastes containing appreciable amounts of organics such as grouted complexant concentrate residues.

Response:

It is assumed in this response that the suggested value of 10.2 gmol/(grout rad) is intended to be 10.2E-13. The current gas generation rate of 3.7E-13 is considered to be sufficiently conservative. However, it can be shown that the gas resulting from a yield of 10.2E-13 can vent through the vents in the catch basin with very small back pressures. See NESHAP documentation for discussion of air pollution. The report is limited to DSSF waste and does not address other waste compositions.

2. The maximum dosage rate is 310 rads per hour at the time of grout pouring. The dose rate declines with the remaining concentrations of cesium-137, which is both a beta and gamma emission source. The use of gamma radiation as the sole basis of predicting radiolytic hydrogen gas formation is incorrect. There is no provision in the estimates for the generation of radiolytic hydrogen gas from the decomposition of organic compounds contained in the grout waste.

Response:

The assumption made is that the yield from beta and gamma radiation are the same. Beta radiation is not neglected.

The presence of organics in the feed can affect the hydrogen generation rate, but the increase is considered to be small due to the low concentration of organics in the feed, and due to the processing that the waste has undergone. See Comments 3 and 19. Also note that Friedman 1985 report that the same amount of organics were included in their DSS waste as are projected to be in the DSSF vaults. Confirmation of gas generation rates is planned, which will include organics in the waste feed.

3. The placement of small vertical tubes in the grout could facilitate the removal of the radiolytic hydrogen gas. The conclusion otherwise is acceptable.

Response:

Gas can move through the grout by diffusion or advection. As noted in the report microcracking of the grout will allow some migration of gas from the grout. Placement of tubes is not considered necessary to allow hydrogen to escape the grout. Preliminary results from gas modeling indicate that it is not desirable to increase gas migration from the grout, it is desirable to have the gas held up in the grout to lower concentrations in the vapor spaces.

4. A passive hydrogen gas venting system from the grout vault may not be adequate. A dynamic gas venting system for both the grout vault top and from the bottom liquid drain has not been considered for removal of the gas from the grout vaults. The rest of this conclusion is acceptable.

Response:

The vault vapor space is normally actively ventilated. The sump area has the capacity to be actively ventilated if necessary.

The existing grout vault passive vent design is adequate to release gas pressure from the vaults, see Comments 2, 3, and 19. Data on the diffusion rate of hydrogen through the asphalt cocoon is currently being collected. Preliminary results indicate that the diffusion rate of gas through the asphalt diffusion barrier is higher than that used in the subject report.

5. This conclusion is acceptable.

Response:

No response required.

6. This conclusion is acceptable except that multiple vents with a diameter of 0.25 inch are necessary.

Response:

The current design includes two vents for each vault with an internal diameter of 0.18 inch. The vents can not act as flame arresters, because maintaining the gas velocity greater than the flame propagation rate because the gas generation rate will decrease as the curie content of the vault decreases. Eventually the decreasing flame rate will allow the flame to propagate back to the vault. The assumption of a spark source 45 feet below ground level in the gravel without conducting equipment in the vicinity is highly questionable. The SAR may choose to evaluate the potential consequences of the soil burn, but the effects appear minor and the spark source incredible.

7. Flammable mixtures of hydrogen and oxygen may also occur in the vault top. These gases should not be allowed to diffuse into the outer soil.

Response:

While filling the vault, the ventilation system will maintain the hydrogen concentration far below flammable compositions. After filling the top of the vault, it will be capped off with a cold grout cap to fill the voids. Therefore, there will not be any void space for hydrogen to collect.

Preliminary results of ongoing studies indicate that the leachate sump will not come to flammable levels in the observation period prior to filling and closing it. The catch basin may come to flammable levels but in the absence of a credible spark source it should not react. If the catch basin somehow does catch fire there is so much mass to cool the gas and so much surface area that a significant event is unlikely.

8. Radon can be removed from the grout vaults if a dynamic exhaust system was used. The radon could then be adsorbed onto the surfaces of an activated carbon adsorption bed.

Response:

The risk from radon release was shown to be negligible, see Comments 26 and 27.

9. Tritium gas could be collected in the suggested exhaust gas system. It could then be oxidized to water by passage through a small incinerator and removed by concentration for isolation. The isolated concentrate would be stored to permit natural decay.

Response:

As discussed in response to Comment 28, the tritium is already expected to be in the water form. Incineration of tritiated water will not provide any degree of control or concentration of tritium.

10. This conclusion is acceptable if gas generation within the vault system is adequately handled.

    Response:

    Agree

31. Recommended Tests, Page 22

    Deficiency:

    The recommended tests are acceptable except that a fourth set of tests should be added to the list.

    Recommendation:

4. The respective rates of gas generation from the differing types of wastes to be grouted need to be determined for at least NCAW, CRW, PFPW, and CCW. A particular concern with regard to hydrogen generation involves those wastes where appreciable levels of organic materials may be present, such as in the complexant concentrate waste (CCW).

    Response:

    The report evaluates only DDSF.

Table 1
Radioactive Isotope Releases from Gases
in the Grouting Vaults

Radioactive isotope	Gas generation, cf/year	Dose commitment, mrem/year
Radon	--	0.0081
Tritium	--	0.0180
Other	--	--
Total	--	--

Table 2
Estimates of Radiolytic Gas Releases
from Grouting Vaults

Specific gases	Alpha emission, gm-mole/gm H_2O·rad	Beta emission, gm mole/gm H_2O·rad	Gamma emission, gm mole/gm H_2O·rad	Total emission, gm-mole/gm H_2O·rad
Hydrogen				
Oxygen				
Tritium				
Nitrous oxide				
Radon				
Other				

Table 3
Effect of Radioactive Emission
on Radiolytic Hydrogen Release

Type of emission	Gas generation, gm-moles H_2/gm H_2O-rad	Reference source
Alpha	23.20×10^{-13}	Gray & Simmons
Beta	?	--
Gamma	7.14×10^{-13}	Gray & Simmons
Total		
Composite	4.51×10^{-13}	Matherson & Ritter
Estimate	47.60×10^{-13}	Author

Table 4
Estimated Sources of Radiolytic Hydrogen
by Type of Radioactive Emission Source

Type of emission	Gas generation, gm-moles H_2/gm H_2O-rad	Percent of total
Alpha	23.20×10^{-13}	48.7
Beta	17.26×10^{-13}	36.3
Gamma	7.14×10^{-13}	15.0
Total	47.60×10^{-13}	100.0

*Estimated by difference.

Table 5
Comparison of Radiolytic Gas Generation
from Simulated Grout Mixtures under Gamma Radiation

Specific factor	Units employed	Bibler tests	Friedman tests
Hydrogen	gm-mole/gm H_2O-rad	1.45×10^{-13}	0.72×10^{-13}
Oxygen	gm-mole/gm H_2O-rad	0.00	0.00
Nitrous oxide	gm-mole/gm H_2O-rad	0.05×10^{-13}	1.89×10^{-13}
Nitrogen	gm-mole/gm H_2O-rad	0.00	0.39×10^{-13}
Total gas*	gm-mole/gm H_2O-rad	1.50×10^{-13}	3.00×10^{-13}
Radiation level	Rad/hour	89,000	800,000
Temperature	°C	41	--
Times	Days	--	11

*Estimated

Table 6
Projected Volumetric Composition of Grout Vault Exhaust Gases

Gas produced	Composition, dry basis, percent	Amount, wet basis, percent
Hydrogen	68.2	64.4
Oxygen	28.7	26.6
Nitrogen	0.6	0.6
Nitrous oxide	3.1	2.9
Dry basis	100.0	94.5
Water vapor	--	5.5
Wet basis	100.0	100.0

Table 7
Reported Literature Values for
Radiolytic Gas Generation

Type of media	Type of emission	Nitrate content	Types of gas generation			Gas generation, gm-mole gas/gm mat-rad	Temperature, °C	Literature source
			H_2	O_2	N_2O			
Water	Alpha	0.0	Not specified			23.20×10^{-13}	--	Gray & Simonson (1985)
	Gamma	0.00	Not specified			7.14×10^{-13}	--	Gray & Simonson (1985)
	Co-60	0.0	Not specified			4.51×10^{-13}	--	Matherson & Ritter (1970)
	Co-60	1.30M	Not specified			0.14×10^{-13}	--	Matherson & Ritter (1970)
Cement-iron oxide	Gamma	0.00	Yes	No	Yes	1.45×10^{-13}	--	Bibler (1978)
	Alpha	0.00	Yes	Yes	Yes	1.33×10^{-13}	--	Bibler (1978)
	Gamma	2.0%	Not specified			0.29×10^{-13}	--	Bibler (1978)
Cement-slag fly ash	Not specified	0.0 (KCl)	Yes	No	Yes	3.65×10^{-13}	--	Lewis & Warren (1989)
Simulated grout	Alpha	Yes	Yes	Yes	Yes	2.49×10^{-13}	--	Friedman (1985)
	Gamma	Yes	Yes	Yes	Yes	0.30×10^{-13}	--	Friedman (1985)

Table 8
Effect of Media Form on Radiolytic Gas Generation

Type of media	Type of emission	Gas generation--gm-mole/gm material-rad		
		Maximum	Minimum	Average
Water	Alpha	--	--	23.20
	Gamma	--	--	7.14
Solid	Alpha	2.49	1.33	1.91
	Gamma	1.45	0.29	0.68

Table 9

Summary of Half-Lives, Decay Energies and Products
for Radioactive Isotopes of Concern
in Grout Solidification Process Reactions[1]

Radioactive Isotope	Half-Life	Decay Energy (MeV/Disintegration)[2]	Decay[3] Mode
Tritium-3	12.26 yrs	0.01861	β_-
Carbon-14	5,730.00 yrs	0.15600	β_-
Cobalt-60	10.50 min	0.05860	β_-, IT
Selenium-79	65,000.00 yrs	0.15400	β_-
Strontium-90	28.10 yrs	0.54600	β_-
Niobium-94	6.26 min	0.0415 (IT) 2.1000 (B)	β_-, IT β_-, IT
Technetium	212,000.00 yrs	0.2920	β_-
Ruthenium-106	367.0 days	0.0394	β_-
Antimony-125	2.70 yrs	0.764	β_-
Iodine-129	17,000,000.00 yrs	0.189	β_-
Cesium-134	2.05 yrs	2.0620	β_-
Cesium-137	30.23 yrs	1.176	β_-
Cerium-144	284.9 days	--.----	β_-
Uranium-234	247,000.00 yrs	4.856	α
Uranium-235	710,000,000.00 yrs	4.681	α, SF
Uranium-238	4,510,0000,000.00 yrs	4.268	α; SF
Neptunium-237	2,140,000.00 yrs	4.956	α
Plutonium-238	86.00 yrs	5.592	α, SF
Plutonium-239	24,400.00 yrs	5.243	α, SF
Plutonium-240	6,580.00 yrs	5.255	α, SF
Americium-241	458.00 yrs	5.640	α
Californium-244	17.60 yrs	5.902	α

[1]Data obtained from Handbook of Chemistry and Physics, 65th Edition, 1984-1985, CRC Press, Inc., Boca Raton, Florida, 1985.

[2]Based on million electron volts (MeV) per disintegration.

[3]Legend: α - Alpha Particle Decay
β - Beta Negative Emission
IT - Isomer Transition
SF - Spontaneous Fission

9-3-85

Table 10
Expected Radioactive Isotope Activity
In a Typical Grouted Waste Mixture

Radioactive Isotope	Activity--Ci/liter		Intensity--watt/liter		Dosage, rads
	Initial (0 yr)	Final (0 yr)	Initial (0 yr)	Final (30 yr)	
Tritium-3	1.14E-05	0.00E+00	--	0.00E+00	4.20E+01
Carbon-14	7.86E-07	7.83E-07	--	2.29E-10	1.31E+01
Cobalt-60	2.00E-05	3.87E-07	--	5.96E-09	4.36E+03
Selenium-79	1.80E-05	1.80E-05	--	4.47E-09	2.55E+02
Strontium-90	7.90E-03	3.82E-03	--	4.43E-06	3.71E+05
Yttrium-90	7.90E-03	3.82E-03	--	2.11E-05	1.77E+06
Niobium-94	2.50E-05	2.50E-05	--	2.54E-07	5.10E+00
Technetium-99	6.40E-05	6.40E-05	--	3.21E-08	1.83E+03
Ruthenium-106	1.20E-02	1.36E-11	--	7.97E-16	4.97E+03
Rhodium-106	1.20E-02	1.36E-11	--	1.20E-13	3.17E+05
Iodine-129	2.20E-07	2.20E-07	--	1.03E-10	5.87E+05
Cesium-134	3.40E-03	1.42E-07	--	1.45E-09	1.96E+07
Cesium-137	2.60E-01	1.31E-01	--	1.32E-04	1.08E+07
Barium-137m	2.46E-01	1.23E-01	--	4.84E-04	3.87E+01
Uranium-238	1.14E-08	1.14E-08	--	2.84E-10	4.62E+03
Plutonium-239	1.20E-06	1.20E-06	--	7.04E-08	4.01E+03
Americium-241	1.40E-06	1.35E-06	--	4.38E-08	2.56E+03
Total			--		5.32E+07

Table 11
Effect of Waste Type on Integrated Radiation Dosage Level
In a Grouting Vault After a 30-Year Storage Period

Radioactive Isotope	HCAW, rads	HCRW, rads	PFPW, rads	CCW, rads	Mixture, rads
Tritium-3	--	--	--	--	4.20E+01
Carbon-14					1.31E+01
Cobalt-60					4.36E+03
Selenium-79					2.55E+02
Strontium-90					3.71E+05
Yttrium-90					1.77E+06
Niobium--94					5.10E+00
Technetium-99					1.83E+03
Ruthenium-106					1.97E+05
Rhodium-106					3.17E+00
Iodine-129					5.87E+05
Cesium-134					1.98E+05
Cesium-137					1.08E+07
Barium-137m					3.87E+07
Uranium-238					1.62E+01
Plutonium-239					4.01E+03
Americium-241					2.56E+03
Total					5.32E+07

Table 12
Estimated Ranges in Radiolytic Gas Generation
from the Grouting Vaults

Estimate number	Gas generation, gm-mole/gm material-rad	Molar flow rate, gm-mole/hour	Volumetric gas flow, cu ft/hour[3]
1	0.14	0.04	0.04
2	3.71×10^{13}	1.01	0.92
3	4.51	1.23	1.12
4	23.20	6.32	5.75
5	47.60	12.96	11.78
Average	7.90[1] 15.77[2]	2.15 4.99	1.95 4.25

Notes:
1. Excludes highest value estimate.
2. Includes highest value estimate.
3. Based on 40°C at 760.0 mm pressure.
4. Based on 9,892 tons of grout occupying 1,791,000 gallons.

Table 13

Summary of Radioactive Isotopes Concentrations
In Waste Feed to the Grout Facility
at the Hanford Site[1,2,3]

Radioactive Isotopes	Concentration (μCi/Liter)	Standard Dev. (μCi/Liter)	Loading (Ci/Million Gal)	Decay mode
Tritium-3	7,000	5,200	26.46	β-
Carbon-14	0.840	0.160	3.18	β-
Cobalt-60	11,000	9,900	41.58	β-,IT
Selenium-79	6,700	11,000	25.33	β-
Strontium-90	6,600,000	2,700,000	24,948.00	β-
Niobium-94	10,000	15,000	37.80	β-,IT
Technetium-99	77,000	7,300	291.06	β-
Ruthenium-106	4,300,000	7,400,000	16,254.00	β-
Iodine-129	0.170	0.079	0.64	β-
Cesium-134	1,200,000	2,100,000	4,536.00	β-
Cesium-137	310,000,000	35,000,000	1,171,800.00	β-
Uranium-234	0.012	0.012	0.05	α
Uranium-235	0.0007	0.0008	0.01	α,SF
Uranium-238	0.0082	0.0046	0.03	α,SF
Neptunium 237	0.058	0.088	0.22	α
Plutonium-239	0.430	0.220	1.63	α,SF
Plutonium-239/240	0.900	0.490	3.40	α,SF
Americium-241	1.400	0.350	5.29	α
Californium-244	0.077	0.099	0.29	α
Total	322,215.5959	---	1,217,974.97	--

Notes:

1. The waste material has a very high total solids level of 290,000 mg/liter and an overall density of 1.50 gm/ml or 10.82 lb/gallon.

2. The total organic content of the liquid is less than 7,000 mg/liter when measured as the sum of the individual constituents, but is much higher than the total organic carbon content of 2.3 mg/liter, as measured.

3. The organic content of the waste liquid comprises less than 3 percent of the total constituent solids present in the waste, and is not sufficient to support its own combustion.

Table 14
Effects of Radiation Dosage Level on
Radiolytic Hydrogen Generation from Grout Mixtures

Radiation emission	Dosage rate, rad/hour	Equilibrium pressure, lb/sq in (psi)
Alpha	400.00	>200
Beta	--	--
Gamma	0.10	20-40*
	27.00	60-110*
	0.89	36
	14.00	200

Table 15
Estimated Values for Molecular Gas
Diffusivity Levels in Asphalt

Gas	Molecular weight, gm/gm-mole	Molecular diffusivity, sq cm/sec
Hydrogen	2	670.6×10^{6}
Oxygen	16	83.8×10^{6}
Carbon dioxide	46	15.0×10^{6}
Radon	222	1.6×10^{6}

DR. MEISEL NOTATIONS

Questions were raised in two TAP meetings, in which we participated, on the possible effects of different radiation sources (α, β, or γ and ^{60}Co used in our experiments as compared to ^{137}Cs, ^{90}Sr or TRUs in 101-SY). In particular, concerns were raised that the H_2 yield in tank 101-SY might be higher than one might expect because of the differences in radiation chemistry from beta or gamma irradiation and that induced by alpha particles. Members of the TAP were also concerned that our γ-source (^{60}Co) radiolysis may not correctly represent the radiolytic conditions in the tank where the sources are mostly β emitters, ^{137}Cs, ^{90}Sr. The following provides the rationale for our contention that the contribution to gas generation from α-radiolysis (TRUs) is negligible and that the difference between the different sources of β and γ-radiolysis is of no consequence.

To address these questions we will:

1. Discuss the physical basis for the difference in radiation chemistry from different ionizing particles.
2. Quantify the different effects expected from the different particles.
3. Make an estimate of the possible G-value difference that can arise from the irradiation between different ionizing particles.
4. Using the estimate of the radionuclides composition (dose rate) in tank 101-SY and the differences estimated in 3), estimate the possible differences in yields.

1. The mechanism for energy deposition is well established to be identical for all ionizing radiation sources. The solution constituents are ionized in proportion to their electron density in the solution. The electrons that are ejected out are thermalized and the radicals and ions are formed in localized regions that are referred to as "spurs." The primary difference among the chemistry arising from different ionizing particles comes from the distance between these spurs along the track of an ionizing particle. In γ-irradiation or on irradiation with high energy electrons (β), the distance between the spurs is approximately 5000 A while the separation between spurs along the path of a 5-MeV α-particle is approximately 200 times shorter (~25 A). At the shorter separation distances between spurs the individual spurs will overlap one another much faster than when the distances are large. Therefore, the closer the spurs are, the higher is the probability that radicals will recombine with one another and the less likely they are to diffuse out to the bulk of the solution and react with other components in the solution. Accordingly, the yield of molecular products (H_2 and H_2O_2) is higher, and the radical yield (H and OH) is lower, if the ionization events are closer together i.e. for α-irradiation relative to β and γ-irradiations.

2. The distance between ionization events can be estimated by the use of a well established and easily accessible parameter, the linear energy transfer (LET), which expresses the amount of energy deposited per unit pathlength of the particle. The larger is the LET, the closer are the ionization events to one another, and thus, the higher is the molecular yield. For ^{60}Co γ rays the LET is 0.23 keV/μm, for ^{137}Cs and ^{90}Sr, the LET is approximately 0.2 keV/μm while for 5.3 MeV α-particle, (typical for the TRUs in the tank) the LET is 46 keV/μm. Thus the ^{60}Co (a γ-source) that we used is an excellent surrogate for the β-emitters, ^{137}Cs and ^{90}Sr. Because the LET of the β emitters from the radionuclides and the γ particles from ^{60}Co are virtually the same, little difference will occur between the surrogate irradiation and that in the tank. The similarity between the effects of β and γ-sources is not surprising once the physical principles the govern the absorption of radiation are understood. The absorption of an energetic γ photon leads to the ejection of a secondary energetic electron (Compton Scattering) from the target molecule. This secondary electron resembles in its energy, and therefore in its effects, a primary electron from a β source. This is the basic reason for the similarity in the LET parameters of ^{60}Co and ^{137}Cs.

We shall refer to high LET (α-emitters) and low LET (β and γ-emitters) particles in the discussion below.

3. No direct measurements of H_2 yields as a function of LET in chemical systems similar to the tank were found in a literature survey that we have conducted. We can, however, estimate the possible G values of H^2 generation from high LET irradiation using the same G-values given in our Annual Report for low LET and making some simplifying assumptions. The G-values for H, H_2, and OH were 0.74, 0.03, and 5.3 respectively can be calculated from Table A1 in our annual report (values of the "Modified" no. of fragments per spur in that table were converted to G-values taking the experimentally observed $G(e^-_{aq}) = 4.8$ and assuming proportion conversion factors for the other species). The value of 5.3 for the G-value of OH is probably too large for reasons given in the annual report; a better estimate is 3.9. The higher value would only decrease the H_2 yield, and so the lower G(OH) estimate allows for a larger margin of safety. The minimum G-value for H_2 at low LET (β or γ) is 0.03. The maximum G-value for H_2 under high LET radiation would be

$$0.03 + \frac{0.74}{2} = 0.4$$ (i.e. all H atoms react with other hydrogen atoms). A more realistic estimate would be to assume that the H atom reacts with either another H atom or with OH radical depending on the concentration of the H to OH. This then means:

$$G(H_2)\,for\ \alpha = 0.03 + 0.74\ x\ \frac{0.74}{(0.74 + 3.9)} = 0.15$$

Thus, the ratio of the yield of H_2 from high LET (α sources) to low LET (β or γ) will be approximately $\frac{0.15}{0.03} = 5$ Even this is a major overestimate because the ionization regions will be separated by ~25 Å for 5 MeV α particle and with the high concentration of chemical scavengers in the system (nitrite), it is highly likely that a large fraction of the H atoms will be scavenged by them rather than generate H_2.

4. The activity in 101-SY from TRUs (average of top, middle, and bottom samples; the following numbers were taken from Table 1 on page 9 of a document labeled 86431-91-008; we do not have the whole document) is less than 30 μC/liter while the activity from the β and γ emitters in the tank is ~7×10^5 μC/liter. From the table of nuclides, one can estimate that the β particles emitted are of approximately 0.5 MeV while the α particles are ~5 MeV. The ratio of the dose deposited by the α - emitters to that deposited by the β - emitters is, thus, approximately $\frac{30 \times 5}{7 \times 10^5 \times 0.5} = 4.3 \times 10^{-4}$. Thus the maximum ratio of H_2 generated from the two types of radiations is:

$$\frac{amount(H_2)\,\alpha}{amount(H_2)\,\beta\text{-}\gamma} = (Ratio\ of\ does\ of\ \frac{\alpha}{\beta\gamma})\ x\ (Ratio\ of\ G(H_2)\ of\ \frac{\alpha}{\beta\text{-}\gamma})$$
$$= 4.3 \times 10^{-4} \times 5 = 2.1 \times 10^{-3}$$

The conclusion is obvious. The yield of hydrogen from the TRUs is negligible in comparison to the yield from the ^{137}Cs; less than 1 percent of the amount that can be generated by the latter. While several approximations were used to make this estimate, they all tend to overestimate $G(H_2)$ from the high LET components (TRUs) in comparison to the low LET components.

ENCLOSURE 2

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LIGHTNING MITIGATION DESIGN

During the November Unit Managers Meeting the subject of lightning protection was discussed. This attachment provides further information concerning lightning protection planned for the grout vaults and associated structures.

Portable Instrument House (PIH):

Three PIHs will be located next to the grout vaults during the operational phase of the vaults. The PIHs will provide high points for lightning contact. The lightning protection system located on these structures conforms to the requirements of NFPA 78, which requires air terminals of lightning protection systems mounted on roofs of gently sloping buildings to project upward in excess of 10-inches above any other roof structure. The ground cable is terminated to the same ground post as the lightning ground connection.

The attached sketch from ECN 129154 shows the current design of the lightning system for PIH number 1. This design will be typical of PIHs 2 and 3.

Exhausters:

All exhausters will have lightning systems which are equal to or surpassing the requirements in NFPA 78. Exhauster stacks will extend more than 25 feet above ground level.

Other Structures:

Other structures in the area include the Grout Processing Facility Dry Materials tower, which is over 50 feet above grade, and well grounded.

Vaults:

During the operational period the top of the concrete grout vault will be buried about 4 feet underground. The vaults are made primarily of concrete with some associated steel risers extending about 6 inches above the asphalt cocoon. The vaults are surrounded by a minimum 3 feet insulating asphalt cocoon layer. This cocoon will provide electrical resistance which will minimize current flow to and from the ground.

When the vault is operational the exhauster and PIHs will be present. The lightning systems of the PIHs and exhauster should allow lightning to preferentially strike them. The PIH and exhauster lightning ground rods will be installed outside of the vault cocoon.

After the operational period the interim closure period begins. During interim closure the vault leachate system is monitored to detect liquid. Early during this approximately 30 years interim closure period the steel

vault risers will either be removed, or buried in cocoon and covered with a 10-foot RCRA closure cover.

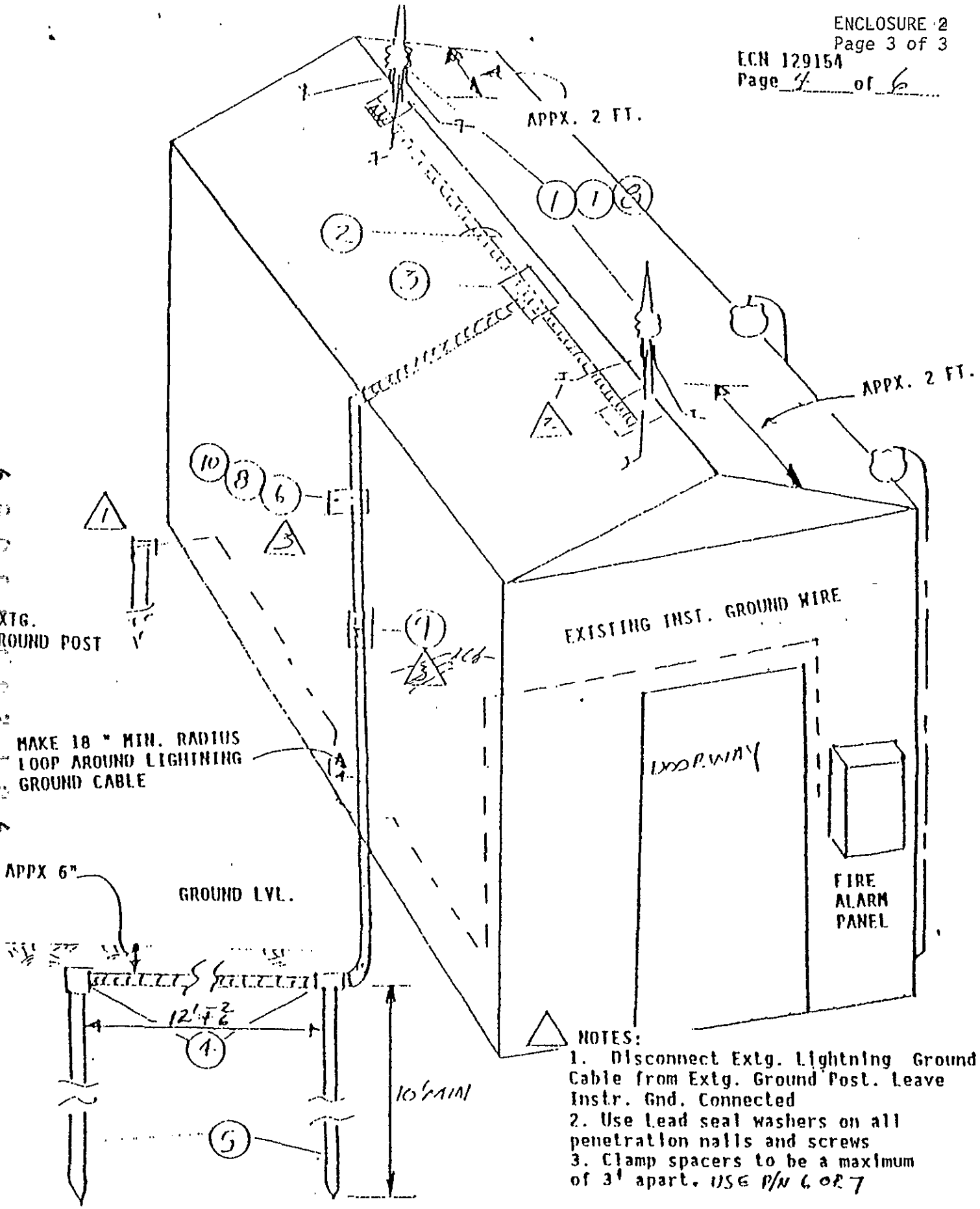
During the interim closure period the leachate sump riser will be the only remaining pipe connection that extends to the RCRA cover surface. Except for periods that the exhauster is attached (if required for sump ventilation) the sump riser will be sealed and present a low receiptor profile for possible lightning strikes.

Instrumentation and pump power supply connections will be located above ground during the interim closure period. They will be grounded outside the vault cocoon.

After the interim closure period the final Hanford barrier will be installed, if necessary. Prior to the Hanford barrier installation the sump riser and sump will be filled, and the insulating cocoon completed. The vault will be sealed about 25 feet below the earth's surface.

The insulating barrier around the vault makes it extremely unlikely that a lightning strike would occur directly on the vault. In the unlikely case of a lightning strike on a piece of equipment, such as an exhauster, it is unlikely that a significant amount of the lightnings' energy would be transmitted to the leachate sump or grout vault, due to better paths (less resistance) to the environment via grounding connections.

The probability of a lightning strike at a time when there is a combustible mixture in a portion of the vault at risk from a lightning strike is very small.



NOTES:
1. Disconnect Extg. Lightning Ground Cable from Extg. Ground Post. Leave Instr. Gnd. Connected
2. Use lead seal washers on all penetration nails and screws
3. Clamp spacers to be a maximum of 3' apart. USE P/N 6 OR 7

SKETCH # 1

LIGHTNING ARRESTOR MODIFICATION--PIR # 1

ENCLOSURE 3

IGNITABLE AND REACTIVE CHARACTERISTICS

Determination of Waste Characteristics

Waste characteristics are determined at the point of generation (see 40 CFR §260 and §261).

It is asserted that the liquid waste is not ignitable or reactive at the point of generation. The action of treatment, in this case solidification, would tend to further reduce or eliminate reactivity or ignitability of waste, unless a waste in solid form were recognizably pyrophoric. By inspection the waste is not pyrophoric.

Ignitability definition WAC 173-303-90:

A solid waste exhibits the characteristic of ignitability if a representative sample of the waste has any of the following properties:

1. **Liquid with a flash point <60°C.** The waste is routinely tested for exotherms below 400°F prior to or during processing in the 242-A evaporator, typically none have been found.

2. **Nonliquid-capable of igniting at STP from; friction, moisture absorption, or spontaneous chemical changes.** None of these ignition scenarios will produce a burn at the point of generation, with either liquid waste or the final solid waste form.

3. **Compressed gas (cylinders)-ignitable per 49 CFR §173.300,** which are DOT requirements. These 49 CFR requirements appear to pertain to transportable compressed gas in cylinders. The waste will not be transported, is not a compressed gas, and is not contained in a gas cylinder.

Reactivity Definition WAC 173-303-090:

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

- **Normally unstable** - the waste and grout are normally stable, most of the waste has been in the tanks many years.

- **Reacts violently with water** - the waste and grout are primarily water, any reaction with water will be minor.

- **Generates toxic gases with water** - the grout mass will not generate a significant amount of gas. The minor amount of gas generated will not be significantly accelerated with the addition of more water.

- **Forms explosive mixtures with water** - this will not occur, as the waste is water based and no waste handling activity, including many which required the addition of water, has resulted in such a response at the point of generation. The intention of this requirement is not to include radiolysis (gas generation induced by radiation) of water, but is more oriented towards, for example, sodium metal reacting with water in a potentially explosive configuration.

- **A cyanide or sulfide waste which generates toxic gas when exposed to pH of 2 to 12.5** - the waste is not a cyanide or sulfide waste, toxic waste constituents released during the disposal action will be in compliance with the requirements of WAC 173-460.

- **Is capable of detonation/explosion if heated under confinement** - no explosive mixture is present at the point of generation.

- **Is capable of detonation or explosive decomposition or reaction at STP, if it is subjected to a strong initiating source** - neither the liquid waste nor the grout will detonate when subjected to a strong initiating source.

- **Forbidden explosive** - the waste and grout are not explosive.

As an extreme example of gas production, municipal landfills produce methane and hydrogen in combustible quantities at much higher rates than anticipated at grout vaults. Municipal landfills are not classified as hazardous waste due to characteristics, i.e., not ignitable or reactive. If gas produced from a disposal action caused the site to be reclassified as characteristic waste due to ignitability or reactivity then many or most municipal landfills would probably also fall into that category. The resultant impacts to waste disposal in the United States could be significant.

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